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GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF LIQUIDS FOR THE ANALYSIS OF METALS

GLA 3015 BG

Revision 3.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of liquids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3015 and 3010M. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr^{6+}). Arsenic (As) and selenium (Se) cannot be analyzed by FLAA.

1.1 MATRICES

This method is applicable to aqueous samples (ground, waste, drinking waters), extracts, and other liquid materials and wastes (such as oil and grease).

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

A representative 5-100 mL portion of sample is digested with nitric acid, or nitric acid and hydrogen peroxide (for As and Se). The digestate is then refluxed with additional nitric acid (GFAAS methods, except for As and Se) or with hydrochoric acid (ICP-OES methods). Aqueous ground waters, extracts, and liquid samples are digested by either standard "hotplate" digestion methods or microwave-assisted digestion methods. Non-aqueous or high dissolved organic containing liquids are digested using the standard hotplate methods, including GLA 3010M, a modified 3010 method. Liquid matrix types include:

- Waters - ground, waste, drinking, other aqueous.
- Extracts - TCLP, SPLP, ASTM D3987-85.
- Miscellaneous - oil, grease, diesel, other.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, ground water versus tank removal waste). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 In the case of methods for total recoverable and/or dissolved metals, digestion is not always required. It should be noted, however, that the less intensive digestion procedure for total recoverable metals may not be sufficiently vigorous to destroy some metal complexes and may therefore give biased results.

4.3 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed. At least quarterly, laboratory dust wipes will be prepared and analyzed. Contamination of more than 500 µg of lead (Pb) per square foot is not permitted.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for *sample receipt into the laboratory.*

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Beakers, Griffin type, 250-mL size.
9.2 Watch covers, ribbed, 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL.
9.4 Glass funnels.
9.5 Filter paper - 15 cm, Whatman 41, or equivalent.
9.6 Sample containers, 50-100 mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
9.9 Microwave digestion apparatus:

- Microwave digestion system, capable of monitoring and maintaining 175°C and/or 70 p.s.i. within digestion vessels, CEM model MDS-2100, or equivalent.
- Lined (polyolefin) digestion vessels, 50-mL size.
- Rupture membranes.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water).
10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% H_2O_2, ACS/analytical reagent grade, Fisher no. H325.
10.5 Spiking standards - GLA-SPK-1A, -3B, 5, and 6, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

Table 1.
Digestion Method Reference Chart.

Analysis	Method Reference	Pre-Digestion Preparation	Microwave Digestions	Standard Digestions			Special Matrices
				ICP/FLAA	GFAA	Special	
Total Metals	SW-846	Preserve with HNO_3 to pH <2	3051A	3010A	3020A	7060A (As) 7740A (se)	3010M for oils, gas, diesel, and waste oil sludges
	EPA		n/a	4.1.3 200.7	4.1.3 200.9	206.2 (As) 270.2 (se)	
	Std Meth		SM-3030-K	SM-3030-F	SM-3030-E		
Dissolved Metals	SW-846	Filter thru 0.45 µ filter, preserve with HNO_3 to pH <2	3015	3010A	3020A	7060A (As) 7740A (Se)	3010M for oils, gas, diesel, and waste oil sludges
	EPA		n/a	4.4.1/4.1.3 200.7	4.1.1/4.1.3 200.9	206.2 (As) 270.2 (Se)	
	Std Meth		SM-3030-K	SM-3030-F	SM3030-E		
Total Recoverable Metals	SW-846	Preserve with HNO_3 to pH <2	n/a	3005	n/a		3005
	EPA		n/a	4.1.4	4.4.4		4.1.4
	Std Meth		n/a	SM-3030-F	SM-3030-F		SM-3030-F

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

CAUTION: All hotplate digestions must be performed in a fume hood.

Table 2.
Procedure Selection Table.

Digestion Type	Analysis Type (1)	Analysis Method	Applicable Method(s)	Digestion Procedure
Microwave	Total Metals Dissolved Metals	Any (2)	SW-846 3015 SM-3030-K	11.4 (MIC)
Standard	Total Metals Dissolved Metals	ICP/FLAA	SW-846 3010A EPA 4.1.3 EPA 200.7 SM-3030-F	11.5 (ICP)
Standard	Total/Dissolved Except As and Se	GFAAS	SW-846 3020A EPA 4.1.3 EPA 200.9 SM-3030-E	11.6 (GF)
Standard	Total/Dissolved As and Se Only	GFAAS	SW-846 7060A (As) SW-846 7740A (Se) EPA 206.2 (As) EPA 270.2 (Se)	11.7 (AS)
Standard	Total Metals	Any (2)	3010M (3)	11.8 (NA)
Standard	Total Recoverable Metals	ICP/FLAA	SW-846 3005 EPA 4.1.4 SM-3030-F	11.9 (A)

(1) Dissolved metals require filtration at time of collection (through a 0.45 μ membrane filter) **prior to preservation**. Chain of custody record should be referenced to determine if sample was properly collected, filtered, and preserved.
(2) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(3) Method 3010M is a GLA method. It is based upon the SW-846 method 3010A, but the addition of hydrochloric acid has been omitted. It is used exclusively for the analysis of metals in oils, oil waste, gas, diesel fuels, and high organic containing waters.

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Method blank - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel.

11.3.2 Laboratory control samples (LCS) - Aliquot 100 mL (45 mL for microwave digestion, section 11.4) of reagent water into a clean digestion vessel. Accurately aliquot 0.2 mL (0.1 for microwave) each of GLA-SPK-1A, -3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels.

11.3.3 Samples - Representative 100 mL (45 mL for microwave digestion, section 11.4) aliquots of samples are aliquoted into clean digestion vessels. For samples with a high solids content (> 1%), a smaller sample size should be used (record the actual volume in the log book).

11.3.4 Matrix spike samples - Measure two additional aliquots 100 mL (45 mL for microwave digestion, section 11.4) of one sample, with volumes similar to the test sample volume, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.2 mL each of GLA-SPK-1A, 3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels. Mark as MS and MSD.

11.4 MICROWAVE-ASSISTED DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS (MIC)

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

11.4.1 Add 5 mL of concentrated HNO_3 to each sample. Stand for 2-10 minutes to allow any vigorous reaction to occur before the vessel is sealed.

11.4.2 The "control vessel" should be selected as the sample appearing to be most reactive. Load the carousel with samples and place in the microwave.

11.4.3 Upon completion of the microwave program, the samples are cooled until the pressure drops below 10 psi (as indicated by the instrument). The pressure sensor is carefully disconnected, temperature probe removed, and the carousel taken out of the instrument.

11.4.4 Each vessel is carefully vented, vent line removed, cap retightened, and shaken to mix.

11.4.5 Each vessel is opened and contents poured into a clean labelled sample cup. If the sample is still warm, or hot, to the touch, it should be cooled further and mixed before analysis. This can be expedited by placing samples in a refrigerator, freezer, or cold water bath for a short time. Observe the volume of each vessel. If loss of sample is apparent (*e.g.* volume less than 50 mL), the sample is discarded and redigested.The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.4.6 Samples are now ready for analysis by ICP, GFAA, or FLAA.

11.5 HOTPLATE DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY ICP-OES (ICP)

NOTE: Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K Na, Tl, V, and Zn.

11.5.1 Add 3 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.5.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.5.4 Add 5 mL of reagent water and 5 mL of concentrated HCl to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.5.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.5.6 The samples are ready for analysis by ICP (or FLAA).

11.6 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY GFAA (GF)

NOTE: Metal analytes for which this digestion is applicable include: Be, Cd, Cr (tot), Pb, Mo, Tl, and V.

11.6.1 Add 3 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.6.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.6.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.6.4 Add 10 mL of reagent water, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.6.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.6 The samples are ready for analysis by GFAAS.

11.7 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS OF As AND Se ONLY BY GFAA (AS)

NOTE: This digestion is applicable only for analysis of arsenic (As) and selenium (Se) by GFAAS.

11.7.1 Add 1 mL of concentrated HNO_3, 2 mL of 30% hydrogen peroxide, and several boiling chips to each sample, cover with watch glasses, and mix.

11.7.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 50 mL. Remove and cool.

11.7.3 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.7.4 The samples are ready for analysis by GFAAS (for As and Se).

11.8 HOTPLATE DIGESTION OF NON-AQUEOUS AND MULTI-PHASE LIQUIDS FOR ANALYSIS BY ICP, GFAA, OR FLAA (NA) - METHOD 3010M

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.8.1 Add 5 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.8.2 Place on a hotplate and maintain at 90-95°C for 15 minutes, or until the volume has been reduced to approximately 10 mL. Remove and cool.

11.8.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool. Add an additional 5 mL of concentrated HNO_3, cover, and heat for an another 30 minutes. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.8.4 Add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.8.5 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.8.6 The samples are ready for analysis by ICP/GFAA/FLAA.

11.9 HOTPLATE DIGESTION OF AQUEOUS AND NON-AQUEOUS LIQUIDS FOR ANALYSIS OF TOTAL RECOVERABLE METALS BY ICP, GFAA, OR FLAA (A)

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.9.1 Add 2 mL of concentrated HNO_3, 5 mL of concentrated HCl, and several boiling chips to each sample, cover with watch glasses, and mix.

11.9.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. **Do not boil samples!** Remove and cool.

11.9.3 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:
- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.9.4 The samples are ready for analysis by ICP/GFAA/FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
13.5 Great Lakes Analytical Quality Assurance Program.
13.6 Great Lakes Analytical Chemical Hygiene Plan.
13.7 Great Lakes Analytical SOP for Login Department.
13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:
- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:
- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

A.2 Section 11.5 (ICP)

EPA Method 200.7:
- Section 11.2.3 - Acid concentrations are made in accordance with SW-846 3010A. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:
- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 Section 11.6 (GF)

EPA Method 200.9:
- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:
- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.4 Section 11.7 (AS)

SW-846 Methods 7060A and 7740A:
- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

EPA 200 Series, Methods 206.2 and 270.2:
- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

A.5 Section 11.8 (NA)

Modified SW-846 Method 3010A (GLA Method 3010M):

- This method parallels SW-846 Method 3010A. The addition of hydrochloric acid has been replaced by addition of 3 mL of nitric acid. This method is used exclusively for the digestion of gasoline, diesel, oil, and oil sludge waste samples, and aqueous samples with a high organic content. These materials show a wide variance of analyte levels and these digestates are analyzed by ICP, GFAAS, or FLAA.
- For non-aqueous or multi-phase samples, a 5-25 g sample is taken, depending upon organic content and allowable regulatory detection levels required. This dilution factor is included in the final calculations of analyte concentrations.

APPENDIX B.

STANDARD SPIKING LEVELS AND VOLUMES.

	Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
	GLA-SPK-1A		0.05/50	0.10/50	0.10/50
	GLA-SPK-3B	0.05/50		0.10/50	0.10/50
	GLA-SPK-4B				
	GLA-SPK-5		0.05/50	0.10/50	0.10/50
	GLA-SPK-6				0.10/50
	EARTH		0.10/50	0.10/50	

Corresponding Elements and Concentrations (mg/L) per Matrix

Set	Element	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
R C R A	Ag	0.005		0.01	0.51
	As	0.015		0.03	0.03
	Ba		0.50	1.0	1.0
	Cd	0.001		0.002	0.502
	Cr	0.003	0.50	1.006	1.006
	Hg	0.001		0.002	0.002
	Pb	0.015		0.03	0.03
	Se	0.015		0.03	0.03
P R I R T Y	Be		0.50	1.0	1.0
	Cu	0.015	0.50	1.03	1.03
	Ni		0.50	1.0	1.0
	Sb	0.015	1.0	2.03	2.03
	Tl	0.015	1.0	2.03	2.03
	Zn		0.50	1.0	1.0
T A L	Al		0.5	1.0	1.0
	Co		0.5	1.0	1.0
	Fe		0.5	1.0	1.0
	Mn		0.5	1.0	1.0
	V		0.5	1.0	1.0
E A R T H	Ca		1.0	1.0	
	K		1.0	1.0	
	Li		1.0	1.0	
	Na		1.0	1.0	
	Mg		1.0	1.0	
E X T R A	B		1.0	2.0	2.0
	Mo		1.0	2.0	2.0
	Si		1.0	2.0	2.0
	Sn		1.0	2.0	2.0
	Ti		1.0	2.0	2.0

APPENDIX B (cont.)

Spiking standard stock solutions :

GLA-SPK-1A

Sb, B, Mo, Si, Sn, Ti	1000 mg/L

GLA-SPK-3B

Sb, As, Cu, Pb, Se, Tl	15 mg/L
Ag	5 mg/L
Cr	3 mg/L
Cd, Hg	1 mg/L

GLA-SPK-4B

Tl	2000 mg/L
Al, Ba, Be, Cd, Cr, Co, Cu,	1000 mg/L
Fe, Pb, Mn, Ni, Ag, V, Zn	1000 mg/L
As, Se	30 mg/L

GLA-SPK-5

Tl	1000 mg/L
Al, Ba, Be, Cr, Co, Cu,	500 mg/L
Fe, Mn, Ni, v, Zn	500 mg/L

GLA-SPK-6

Cd, Ag	250 mg/L

CLPP-ICS-A

Al, Ca, Mg	5000 mg/L
Fe	2000 mg/L

EARTH METALS

Ca, Mg, K, Na	10000 mg/L

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

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STANDARD OPERATING PROCEDURE (018)
METHOD CLARIFICTION

Date Effective: 12/1/98 Supersedes: 10/1/93

Method No.: EPA 200.7 Method Title: Liquid extractions for FLAA / ICP

The above method is currently being used with the following clarificationstions:

Liquid extractions for ICP and FLAA are being compliled into one extraction called EPA 200.7. This was done as a time saving measure for sample preparation. Two millilite of concentrated HNO3 and five milliliters of concentrated HCL are added to each 100 mil of sample. Each sample is then gently heated, not boiled until a volume of approximately 20 ml has been reached. Ribbed watch glass are used during this process. Afterwards, each sample is allowed to cool and is then filtered to a final volume of 100 ml with deionized water. This method takes the place of EPA Methods 200.7, 3005, and 3010.

The following have been added to the analyte list:

Germanium	CAS No.:	7440-56-4
Tantalum	CAS No.:	7440-25-7

Approved: _____ Date: 2-1-98

NOTE: The above information reflects current modifications to the method. Please reference the specific section modified through the numerical designation used by the procedure and give a brief explaination why the modification has been made.

METHOD #: 3010A (SW-846 Update I, July 1992)

TITLE: Acid Digestion Of Aqueous Samples And Extracts For Total Metals For Analysis By FLAA Or ICP Spectroscopy

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FL M) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010A may be analyzed by FLAA or ICP for the following:

ANALYTE:	CAS #
Aluminum Al	7429-90-5
Arsenic (*) As	7440-38-2
Barium Ba	7440-39-3
Beryllium Be	7440-41-7
Cadmium Cd	7440-43-9
Calcium Ca	7440-70-2
Chromium Cr	7440-47-3
Cobalt Co	7440-48-4
Copper Cu	7440-50-8
Iron Fe	7439-89-6
Lead Pb	7439-92-1
Magnesium Mg	7439-95-4
Manganese Mn	7439-96-5
Molybdenum Mo	7439-98-7
Nickel Ni	7440-02-0
Potassium K	7440-09-7
Selenium (*)	7782-49-2

Se		
Sodium		7440-23-5
Na		
Thallium		7440-28-0
Tl		
Vanadium		7440-62-2
V		
Zinc		7440-66-6
Zn		

(*) Analysis by ICP

INSTRUMENTATION: N/A

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.
4.2 Watch glasses - Ribbed and plain or equivalent.
4.3 Qualitative filter paper or centrifugation equipment.
4.4 Graduated cylinder or equivalent - 100mL.
4.5 Funnel or equivalent.
4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95-C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the

specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO3. Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

[NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.]

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when

necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks (calibration and reagent) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. Refer to Chapter One for proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000A, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample that is suspected of having an interference.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals. American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

Copy #: 3050-_____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF SOLIDS FOR THE ANALYSIS OF METALS

GLA 3050 BG

Revision 3.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of solids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3050B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr^{6+}).

1.1 MATRICES

This method is applicable to soils, solids (such as wipes and paints), sediments, and sludges. This method is a very strong acid digestion that will dissolve almost all elements; however, silicate structures are not normally dissolved.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide, and then refluxed with additional nitric (for SW-846 method 3050B) or nitric/hydrochoric acids (EPA method 200.7). The digestate is then filtered and diluted for analysis by ICP, GFAAS, and/or FLAA. A separate sample is dried if necessary for dry weight calculations. Solid matrix types and amounts used include:

- Soils and sediments - 1-2 g portion.
- Paint chips - up to 2 g.
- Paint or dust wipes and filters - entire wipe or filter (including washings).
- Waste sludges - a larger portion may be taken based upon the dry weight, up to 2 g of solid.
- Miscellaneous - mixed solids, waste oil sludges (may require particle size reduction and sub-sampling).

The approximate linear upper ranges for a 2-g sample size are:

- As, Be, Cd, Co, Cr, Cu, Mo, Ni, Se, Tl, V, Zn - 1,000,000 mg/kg.
- Pb, Sb - 200,000 mg/kg.
- Ag, Ba - 2500 mg/kg.

Smaller sample sizes should be taken if limits are exceeded.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, soil versus water treatment waste sludge). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- *An error in a previously reported sample is discovered.*

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Beakers, Griffin type, 250-mL size.
9.2 Watch covers, ribbed, 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL (wide mouth).
9.4 Glass funnels.
9.5 Filter paper - 9 and 15 cm, Whatman 41, or equivalent.
9.6 Sample containers, 50 or 100-mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
9.9 Hot block digestion apparatus:

- HotBlock, Environmental Systems, set to maintain a sample temperature of 90-95°C.
- Polyolefin digestion vessels, 50-mL size, with watch covers and snap-on caps.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water).
10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% H_2O_2, ACS/analytical reagent grade, Fisher no. H325. **CAUTION:** Hydrogen peroxide is an oxidizer.
10.5 Spiking standards - GLA-SPK-1A and -4B, Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

Table 1.
Digestion Method Reference Chart.

Analysis	Method Reference	Microwave Digestions	Standard Digestions		
			ICP/FLAA	GFAA	Special
Total Metals	SW-846	3051A	3050B + HCl	3050B + HNO_3	7060A (As) 7740A (Se)
	EPA	n/a	200.7	200.9	206.2 (As) 270.2 (Se)
Air Filters	NIOSH	n/a	7082	7082	n/a

Table 2.
Procedure Selection Table.

Digestion Type	Analysis Type	Analysis Method	Applicable Method(s)	Digestion Procedure
Standard	Total Metals	Any (1)	SW-846 3050B EPA 200.9 (3)	11.4 (GEN)
Standard	Air Filter - Lead Only	Any (1)	NIOSH 7082	11.4 (GEN)
Standard	Total Metals (2)	ICP/FLAA	SW-846 3050B EPA 200.7 (4)	11.5 (ICP)
HotBlock	Total Metals	Any (1)	SW-846 3050B	11.6 (HB)

(1) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(2) For samples requiring addition of hydrochloric acid. This procedure produces digestates which can only be analyzed by ICP-OES.
(3) Samples are refluxed with nitric acid for metals determination by all analytical methods.
(4) Samples are refluxed with hydrochloric acid for metals determination by ICP-OES only.

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

CAUTION: All hotplate digestions must be performed in a fume hood.

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Soil, sediment, and other solid samples:

- Samples - A representative 2.0g +/- 0.01g (1.0 g for hotblock digestion, section 11.6) aliquot is weighed into a clean beaker (or digestion tube for hotblock digestion).
- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the sample replicates, and mark them as MS and MSD.
- LCS – Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the solution, and mark the sample as LCS.

Note: If requested, the sample weight can be based on dry-weight –corrected soil.. Refer to SOP GLA160BG for instructions on determining dry weight.

11.3.2 Sludge/high water content samples:

- Samples - Each sample should be well mixed before taking a representative portion for digestion. If the sample contains significant water, upon client request, a dry weight determination may be performed prior to digestion (See SOP GLA160BG for dry weight determination), and the sample size adjusted and/or calculated as follows:

$$\textit{sample weight (g)} = \frac{\textit{2.0 (1.0 for hotblock) g}}{\textit{dry weight (as decimal percent)}}$$

- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the sample replicates. Add 5 mL of reagent water to each, washing the spike solutions into the beakers or vessels. Mark as MS and MSD.
- LCS – Combine 7.5ml of reagent water and 7.5ml of nitric acid. Accurately aliquot 0.05ml each of GLA-SPK-1A, -4B, As/Se Soln., and -EM into the solution, and mark the sample as LCS.

11.3.3 Wipes samples (surrogate matrix QC):

- Samples - Transfer the entire wipe into a clean beaker along with any liquid and/or loose material which has fallen off the wipe. Rinse the sample container with three successive portions of reagent water, adding each rinsate to the beaker.
- Surrogate matrix blank - Place a 9- or 15-cm Whatman 41 filter paper into a clean beaker. Add 15 mL of reagent water.
- LCS - Place 9- or 15-cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.3.4 Paint/paint dust samples:

- Samples - Weigh as large a portion as possible, up to 2 g (accurately to the nearest 0.0001 g), into a clean beaker. Record the weight(s) in the log book.
- Surrogate matrix spike samples - Place 9 (or 15) cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.4 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (GEN)

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

11.4.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watchglasses, and mix.

11.4.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.

11.4.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.4.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.4.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

11.4.6 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. If samples are to be analyzed immediately, filter the digestate through a Whatman 41 filter paper into a metal-free container. Otherwise, samples may be allowed to settle 1 hour, or overnight, prior to analysis. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.4.7 The samples are ready for analysis by ICP, GFAAS, or FLAA.

11.5 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES OR FLAA ONLY (ICP)

NOTE: Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn.

11.5.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.

11.5.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.5.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.5.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

11.5.6 Add 5 mL of concentrated HCl and 10 mL of reagent water to each sample. Cover and return to hotplate for 15 minutes. Remove and cool.

11.5.7 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. Filter the digestate through a Whatman 41 filter paper into a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.5.8 The samples are ready for analysis by ICP or FLAA.

11.6 HOTBLOCK DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (HB)

NOTE: Metal analytes for which this digestion is applicable include:
Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

NOTE: This procedure is not applicable for wipes samples.

11.6.1 Add 5 mL of reagent water (except for wipes samples) and 7.5 mL of concentrated HNO_3, to each sample. Cover and mix.

11.6.2 Place in digestor and heat for 75 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.3 After the samples have cooled, slowly and carefully add 1 mL of 30% hydrogen peroxide to each. Allow vigorous reaction to subside. Place in digestor and heat for 15 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.4 Bring total sample volumes to 50 mL each with reagent water, cover and mix. Allow samples to settle at least 1 hour (or overnight). If immediate analysis is required, samples may be filtered through Whatman 41 filter paper. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.5 The samples are ready for analysis by ICP, GFAAS, or FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
13.5 NIOSH Method 7082: Analysis of Lead in Air Filters.
13.6 Great Lakes Analytical Quality Assurance Program.
13.7 Great Lakes Analytical Chemical Hygiene Plan.
13.8 Great Lakes Analytical SOP for Login Department.
13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

A.2 Section 11.4 - Sample Digestion (GEN)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 Section 11.5 - Sample Digestion (ICP)

EPA Method 200.9:

- Section 11.3.3 - The addition of hydrochloric acid has been omitted an additional addition of nitric acid made its place. The interferences associated with chloride in the graphite furnace analysis are well documented in many reference documents (for example, EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

APPENDIX B.

STANDARD SPIKING LEVELS AND VOLUMES.

	Standard	Aliquot/Volume
	GLA-SPK-1A	0.10/100
	GLA-SPK-4B	0.10/100
	As/Se	0.05/50
	EARTH	0.05/100

Corresponding Elements and Concentrations (mg/Kg)

Set	*Element*	*Soil/Solid*
R C R A	Ag	1.0
	As	0.53
	Ba	1.0
	Cd	1.0
	Cr	1.0
	Hg	
	Pb	1.0
	Se	0.28
P R I R T Y	Be	1.0
	Cu	1.0
	Ni	1.0
	Sb	1.0
	Tl	2.0
	Zn	1.0
T A L	Al	1.0
	Co	1.0
	Fe	1.0
	Mn	1.0
	V	1.0
E A R T H	Ca	1.0
	K	1.0
	Li	1.0
	Na	1.0
	Mg	1.0
E X T R A	B	1.0
	Mo	1.0
	Si	1.0
	Sn	1.0
	Ti	1.0

APPENDIX B (cont.)

Spiking standard stock solutions :

GLA-SPK-1A

Sb, B, Mo, Si, Sn, Ti	1000 mg/L

GLA-SPK-4B

Tl	2000 mg/L
Al, Ba, Be, Cd, Cr, Co, Cu,	1000 mg/L
Fe, Pb, Mn, Ni, Ag, V, Zn	1000 mg/L
As, Se	30 mg/L

EARTH METALS

Ca, Mg, K, Na	10000 mg/L

As/Se Solution

As, Se	1000 mg/L

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

Sequoia Analytical

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819 Striker Avenue, Suite 8, Sacramento, CA 95834, (916) 921-9600, FAX (916) 921-0100
1455 McDowell Blvd. North, Ste. D, Petaluma, CA 94954, (707) 792-1865, FAX (707) 792-0342
1551 Industrial Road, San Carlos, CA 94070-4111, (650) 232-9600, FAX (650) 232-9612

STANDARD OPERATING PROCEDURE (018a)
METHOD CLARIFICTION

Date Effective: 12/1/98 Supersedes: 9/1/91

Method No.: EPA 3050A Method Title: Solids extractions for FLAA / ICP

The above method is currently being used with the following clarificationstions:

The top one inch in eaach soil tube is discarded and a small amount of sample is mixed since multiple analyses would be required using the same soil cores, including volatile organic tests. To get better homogeneity, soil cores would have to be taken for inorganic analyses separately from those for volatile organics.

The following have been added to the analyte list:

Germanium	CAS No.:	7440-56-4
Tantalum	CAS No.:	7440-25-7

Approved: _____ Date: 12-1-98

NOTE: The above information reflects current modifications to the method. Please reference the specific section modified through the numerical designation used by the procedure and give a brief explaination why the modification has been made.

METHOD #: 3050A (SW-846 Update I, July 1992)

TITLE: Acid Digestion Of Sediments, Sludges, And Soils

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

ANALYTE:	CAS #
FLAA	
Aluminum Al	7440-36-0
Barium Ba	7440-39-3
Beryllium Be	7440-41-7
Cadmium Cd	7440-43-9
Calcium Ca	7440-70-2
Chromium Cr	7440-43-9
Cobalt Co	7440-48-4
Copper Cu	7440-50-8
Iron Fe	7439-89-6
Lead Pb	7439-92-1
Magnesium Mg	7439-95-4
Manganese Mn	7439-96-5
Molybdenum Mo	7439-98-7
Nickel Ni	7440-02-0
Osmium Os	7440-04-2
Potassium K	7440-09-7
Silver	7440-22-4

Ag	
Sodium	7440-23-5
Na	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	
Zinc	7440-66-6
Zn	

GFAA

Arsenic	7440-38-2
As	
Beryllium	7440-41-7
Be	
Cadmium	7440-43-9
Cd	
Chromium	7440-43-9
Cr	
Cobalt	7440-48-4
Co	
Iron	7439-89-6
Fe	
Lead	7439-92-1
Pb	
Molybdenum	7439-98-7
Mo	
Selenium	7782-49-2
Se	
Thallium	7440-28-0
Tl	
Vanadium	7440-62-2
V	

[NOTE See Method 7760 for FLAA preparation for Silver.]

INSTRUMENTATION: N/A

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses and nitric acid is used for furnace AA work. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl,

and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total % solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers - 250-mL, or equivalent.
4.2 Watch glasses ribbed or equivalent.
4.3 Drying ovens - That can be maintained at 30-C.
4.4 Thermometer - That covers range of 0-200-C.
.5 Filter paper - Whatman No. 41 or equivalent.
4.6 Centrifuge and centrifuge tubes.
4.7 Analytical Balance - Capable of accurately weighing to the nearest 0.01 g.
4.8 Electric Hot Plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95-C.
4.9 Glass Funnel or equivalent.
4.10 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.
5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.
5.3 Nitric acid (concentrated), HNO3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.
5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.
5.4 Hydrogen peroxide (30%), H2O2. Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample. For samples with low percent solids a larger sample size may be used as long as digestion is completed.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95-C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

[NOTE: Do not add more than a total of 10 mL 30% H_2O_2.]

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to a 100 mL volume with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for

analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, preparation blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.
3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.

Copy #: 7000-____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING GFAA

GLA 7000 BG

Revision 2.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of samples for trace metal content by graphite furnace atomic absorption (GFAA). The procedure for digestion of liquids is GLA 3015 BG, and for the digestion of solids is GLA 3050 BG. This SOP is an interpretation of EPA Method 200.9, Standard Methods no. 3113, Section B, and SW-846 no. 7000A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for GFAA analysis from GLA 3015 BG and GLA 3050 BG. Samples must be analyzed within 6 months (liquids preserved with nitric acid). Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

Aliquots of the digested samples are spiked with a matrix modifier and placed in the graphite tube via the instrument autosampler. First, a low current heats the tube to dry the sample. The second, or charring stage, destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the samples. The resultant ground-state atomic vapor absorbs radiation from the hollow cathode lamp, the absorption proportional to the analyte concentration. (See Appendix A for method exceptions.)

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 GRAPHITE FURNACE

The graphite furnace produces ultraviolet radiation. Do not view directly. The magnet of the furnace produces a field of about 8000 gauss RMS during the read stage. Keep pacemakers and magnetic storage media at a minimum distance of 30 cm (12 inches).

4.0 INTERFERENCES

4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.

4.2 Elemental arsenic and selenium, as well as many of their compounds, are volatile. Samples are susceptible to analyte loss during digestion. Spiked samples are employed to determine whether proper digestion procedures were followed.

4.3 Non-specific absorption and light scattering can occur during analyses for arsenic and selenium during the atomization step. Zeeman background correction is used to minimize this effect.

4.4 Chlorides (>800 ppm) and sulfate (>200 ppm) interfere with the analysis of selenium. The addition of nickel nitrate as the matrix modifier decreases this interference.

4.5 Sometimes an analyte is not completely volatilized and removed from the furnace. This can result in carryover which may be detected by analyses of blanks, and can be decreased by operating the furnace at full power at periodic intervals.

4.6 Chemical reaction of elements in the sample with graphite may occur at high temperatures. Elements that form carbides are barium, molybdenum, nickel, silicon, titanium, and vanadium. Using pryolytically coated tubes minimizes this problem.

4.7 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with 50% nitric acid and DI water (see Appendix B). Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 *GFAA Log Book:*

A log book will be maintained for all metals analyses performed on the GFAA. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Sample matrix type
- GLA Sample I.D. (one complete for each set)
- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.

5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples. (See Appendix C for information on spike volumes and concentrations.)

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within **15%** of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

NOTE: For TCLP extracts, the sample matrix spike for As and Se (only) must be at least 50%. Other limits may be applicable per client request. If the recovery falls below this level, the method of standard additions must be used.

6.5 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.6 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for *sample receipt into the laboratory.*

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory *Information Management System (LIMS). The system is checked daily and a hard copy* generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- *Copies of all method detection limit studies and dates in use.*
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the GFAA instrument is calibrated at least daily, per each matrix analyzed, and the calibration checked using a Check Standard. The concentrations of the Check Standards must pass within limits indicated in Table 2 (within 10% of the expected values initially, and within 20% thereafter, after every 10 samples).

8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.

- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Atomic Absorption Spectrophotometer, Varian SpectrAA-600Z, computer controlled, with Zeeman correction capacity, or equivalent .
9.2 Graphite tube atomizer - GTA 100Z, or equivalent.
9.3 Refrigerated water recirculator - set at 20-25°C, Coolflow CFT-33, or equivalent.
9.4 Four position lamp turrent.
9.5 Graphite tubes - pyrolytic coated partition tubes; except use L'vov platform tubes for cadmium analyses.
9.6 Autosampler, programmable - PSD 97Z, 50 position, or equivalent.
9.7 Volumetric flasks, 25-100 mL.
9.8 Volumetric pipettors, adjustable volume.
9.9 Sample containers, minimum 100-mL capacity, metal-free.
9.10 Analytical balance, calibrated.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water).
10.2 Argon gas source at 41 psi.
10.3 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.4 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.5 Sulfuric acid - concentrated H_2SO_4, ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.6 Calibration standards - 1000 ppm, for individual analytes, from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific. Prepare stock standard containing 3-6 ppm of analytes of interest, then working standards of 6-60 ppb (see Table 1).
10.7 Check standard - 30 ppb, for mid-range concentration. Preparation similarly to standard 10.5.
10.8 2% Palladium in nitric acid solution - VHG Labs no. xxx.
10.9 1% Nickel in nitric acid solution - VHG Labs no. xxx.
10.10 Citric acid - reagent grade, xxx no. xxx.
10.11 Ammonium phosphate, dibasic - $(NH_4)_2HPO_4$, Fisher no. xxx.
10.13 Matrix modifiers - for general analytes, use palladium/nickel/citric acid solution. Use appropriate modifiers when necessary for cadmium and silver.
Mixed modifier solution for As, Se, Pb: Aliquot 20 mL of 2% palladium solution, 10 mL of 1% nickel solution, 0.50 g of citric acid and dilute to 100 mL with reagent water.
Phosphate modifier for Cd: Dissolve 1 g of $(NH_4)_2HPO_4$ in 100 mL of reagent water.
Palladium modifier for Ag: Dilute 20 mL of 2% palladium solution to 100 mL with reagent water.

Table 1. **Digestion Methods and Standard Preparations.**		
MATRIX	DIGESTION METHOD	STANDARD PREPARED IN
Water Waste water Ground Water ASTM Leachate	3015	10% nitric acid in reagent water
Soil Sludge Solid Wipes Sludge waste Non-aqueous liquids	3050B 3010M	15% nitric acid in reagent water
TCLP Fluid 1	3015	10% nitric acid in TCLP Fluid 1
TCLP Fluid 2	3015	10% nitric acid in TCLP Fluid 2
SPLP Fluid 1	3015	10% nitric acid in SPLP Fluid 1
SPLP Fluid 2	3015	10% nitric acid in SPLP Fluid 2
Air filters	NIOSH 7082	15% nitric acid in reagent water

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: Metal analytes for which this method is applicable include: Sb, As, Ba, Cd, Cr, Cu, Pb, Se, Ag, and Tl. (See Appendix D for example wavelengths, instrument detection limits, and concentration ranges.)

11.1 INSTRUMENT PARAMETERS

The following are general instrument parameters. There is a specific hallow cathode lamp for each element. For more detail, consult the manufacturer's operation manual, the maintenance logbook, and the computer generated methods.

11.1.1 Flame Analyses

Parameter	**Mn**	**Fe**	**K**	**Cr^{6+}**
Wavelength	279.5	248.3	766.5	357.9
Fuel	Acetylene	Acetylene	Acetylene	Acetylene
Oxidant	Air	Air	Air	Nitrous Oxide
Type of flame	Slightly oxidizing	Slightly oxidizing	Slightly oxidizing	Fuel Rich
Background correction	Yes	Yes	No	No

11.1.2 Furnace Analyses

Parameter	Pb	As	Se	Tl	Sb	Cd	Cr
Drying Time (sec)/ Temp (°C)	30/120	30/120	30/120	30/120	30/120	30/120	30/120
Ashing Time (sec)/ Temp (°C)	15/800	15/1100	20/900	15/400	20/500	15/400	16/1000
Atomizing Time (sec)/ Temp (°C)	4/2300	5.5/2400	4.1/2400	5.0/2000	5.7/2200	6.0/1600	6.4/2600
Purge Gas	Argon	Argon	Argon	Argon	Argon	Argon	Argon
Wavelength	283.3	193.7	196.0	276.8	217.6	228.8	357.9
Background Corr.	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Note: The above parameters are general. These values could change in order to optimize the instrument for different matrices and other elements.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***. The user's manual for the instrument can be consulted for more details on operation of the instrument.

11.2 INSTRUMENT CALIBRATION

11.2.1 The GFAA is calibrated daily before samples are analyzed in accordance with the instrument manufacturer's instructions. The standard curve includes one blank and a minimum of three standards, the lowest at or near the method detection limit. Most elements are calibrated using standard concentrations of 10, 20, 40, and 60 µg/L. The calibration must pass with correlation coefficients, r^2, of at least 0.9950. The instrument performs two attempts to pass calibration before automatically pausing the run.

11.2.2 The calibration is checked using a Check Standard initially and after every 10 samples. The recovery of the analytes in the Check Standard must be within 10% of expected values initially, and within 20% thereafter.

11.3 ANALYSIS OF SAMPLES

11.3.1 A sequence of QC and test samples is prepared and analyzed:

1. Calibration blank
2. Check standard
3. Check standard
4. High standard
5. Calibration blank
6. 10 Samples
7. Check standard
8. Calibration blank
9. 10 Samples

Note: Each analytical run must end with a calibration blank and a check standard.

Table 2: **Acceptance Criteria for Check Samples**

Calibration blank	< reporting limit
Check standard	±10%, unless second check standard passes
Check standard	±10%, unless first check standard passes
High standard	+10%
Calibration blank	< reporting limit
Continuing check - CCV	±20%
- CCB	< reporting limit

If any parameter fails, the problem must be corrected and tests passed before continuing with samples, including possibly recalibrating the instrument.

11.3.2 A standard is run periodically to gauge the lifetime and performance of the graphite tubes. A lack of reproducibility, or a change in the signal for the standard, indicates that tube replacement is due. The ordinary life of a pyrolytic coated graphite tube is approximately 100-350 firings, depending upon the sample matrix and analyte.

11.3.3 If the concentration of a sample is greater than the highest standard plus 10%, the sample must be diluted and re-analyzed. The instrument automatically dilutes samples 1:4 and 1:24. If results are still out of range, manual dilutions must be performed.

11.3.4 Background correction (Zeeman) must be incorporated at all times. Background correction is important during flameless atomization, especially at wavelengths below 350 nm, and particularly for the analysis of arsenic and selenium in the presence of iron. False positive results may occur from the absorption or scattering of light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam.

11.3.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where: C_x = Concentration of the sample
S_B = The analytical signal for the sample and water solution (corrected for the blank)
V_S = Volume of the standard solution added
C_S = Concentration of the standard solution added
S_A = The analytical signal for the sample and standard solution (corrected for the blank)
V_S = Volume of the sample added to each solution.

Note: V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X , and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

11.4 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported.

11.4.1 Liquid Samples:

mg/L = analyzed concentration × dilution factor

Note: For liquids digested using the microwave method, multiply concentrations by the factor 50/45 (= 1.11) to account for dilution of 45 mL of sample with 5 mL of nitric acid.

11.4.2 Solid Samples:

mg/kg =analyzed concentration × dilution factor

For solids, multiply concentrations by the factor 100/2 (= 50) to convert from mg/L to mg/kg of sample (from 2 g digested to 100 mL solution, or 1 g to 50 mL for HotBlock digestions). If the sample weight differs substantially from 2 g (or 1 g), use the factor 100/weight (or 50/weight) instead.

11.4.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.4.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. (See Appendix B.) Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 GRAPHITE FURNACE

The graphite shield (shroud) and chimney should be cleaned each time the graphite tube is replaced, using methanol.

The quartz windows should be regularly inspected. To clean, gently remove the windows, wash with 30% methanol, and dry with a Kimwipe. Never use coarse cloths or abrasive cleaning solutions.

The autosampler capillary and syringe should be inspected periodically for wear and damage. Repair or replace when required. Similarly, inspect and replace the electrodes when necessary (for example, when the absorbance peak for a standard begins to shift).

13.0 REFERENCES

13.1 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.2 Method 3113: Metals by Electrothermal Atomic Absorption Spectrometry, Section B (Electrothermal Atomic Absorption Spectrometric Method); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Method SW-846, 7000: Atomic Absorption Methods.
13.4 Great Lakes Analytical Quality Assurance Program.
13.5 Great Lakes Analytical Chemical Hygiene Plan.
13.6 Great Lakes Analytical SOP for Login Department.
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual

APPENDIX A.

METHOD EXCEPTIONS.

A.1 EPA Method 200.9:

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

A.2 SM-3030-E:

Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 SW-846 Methods 7060A and 7740A:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

A.4 EPA 200 Series, Methods 206.2 and 270.2:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

APPENDIX B.

GLASSWARE PREPARATION FOR METAL ANALYSES.

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

B.1 All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

B.2 Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

B.3 All glassware shall subsequently be hand-washed using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

B.4 All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

APPENDIX C.

STANDARD SPIKING LEVELS AND VOLUMES.

	Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
	GLA-SPK-1A	0.10/100		0.05/50	0.10/50	0.10/50
	GLA-SPK-3B		0.05/50		0.10/50	0.10/50
	GLA-SPK-4B	0.10/100				
	GLA-SPK-5			0.05/50	0.10/50	0.10/50
	GLA-SPK-6					0.10/50
	As/Se Soln.	0.05/50				
	EARTH	0.10/100		0.05/50	0.05/50	

Corresponding Elements and Concentrations (ppm) per matrix

Set	Element	Solid/Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
RCRA	Ag	1.0	0.005		0.01	0.51
	As	0.53	0.015		0.03	0.03
	Ba	1.0		0.50	1.0	1.0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.001	0.001
	Pb	1.0	0.015		0.03	0.03
	Se	0.28	0.015		0.03	0.03
PRIRTY	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1.0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2.03
	Zn	1.0		0.50	1.0	1.0
TAL	Al	1.0		0.5	1.0	1.0
	Co	1.0		0.5	1.0	1.0
	Fe	1.0		0.5	1.0	1.0
	Mn	1.0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0
EARTH	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1.0	1.0	
	Mg	1.0		1.0	1.0	
EXTRA	B	1.0		1.0	2.0	2.0
	Mo	1.0		1.0	2.0	2.0
	Si	1.0		1.0	2.0	2.0
	Sn	1.0		1.0	2.0	2.0
	Ti	1.0		1.0	2.0	2.0

APPENDIX D.

EXAMPLE WAVELENGTHS, DETECTION LEVELS, AND CONCENTRATION RANGES FOR GFAA.

Element	Wavelength (nm)	IDL (µg/L)	Conc Range (µg/L)
Aluminum (Al)	309.3	3	20-200
Antimony (Sb)	217.6	3	20-300
Arsenic (As)	193.7	1	5-100
Barium (Ba)	553.6	2	10-200
Beryllium (Be)	234.9	0.2	1-30
Cadmium (Cd)	228.8	2	0.5-10
Chromium (Cr)	357.9	1	5-100
Cobalt (Co)	240.7	1	5-100
Copper (Cu)	324.7	1	5-100
Iron (Fe)	248.3	1	5-100
Lead (Pb)†	283.3	1	5-100
Manganese (Mn)	279.5	0.2	1-30
Molybdenum (Mo)	313.3	1	3-60
Nickel (Ni)	232.0	1	5-100
Selenium (Se)	196.0	2	5-100
Silver (Ag)	328.1	0.2	1-25
Tin (Sn)	224.6	5	20-300

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

Copy #: 6010-____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING ICP

GLA 6010 BG

Revision 2.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for analsis of samples for trace metal content by ICP-OES. The procedure for the digestion of liquids is GLA 3015 BG, and for the digestion of solids GLA 3050 BG. This SOP is an interpretation of EPA Methods 200.7, Standard Methods no. 3020, and SW-846 no. 6010B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for ICP analysis from GLA 3015 BG and GLA 3050 BG. Samples are to be analyzed for metals within 6 months. Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

This method describes a technique for the simultaneous (or sequential) multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the ICP plasma torch where excitation occurs. The plasma torch consists of a flowing stream of argon which is ionized by an applied radio frequency of about 1.1 KW power (0.95-1.15 KW at 27-41 MHz). The field is inductively coupled to the ionized gas by a water cooled coil. Characteristic atomic-line emission spectra are produced by the high temperatures of the plasma torch (6000-8000 K). The spectra are dispersed by a grating spectrophotometer and the intensities of the lines are monitored by photomultiplier tubes. The currents from the photomultiplier tubes are controlled and processed by a computer system. A background correction technique is required to compensate for variable background contributions to the determination of trace elements.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 PLASMA TORCH

The ICP plasma torch produces temperatures of 6000-8000 K and high levels of ultraviolet radiation. All instrument safety interlocks and shields must be in place and operational at all times.

4.0 INTERFERENCES

4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.

4.2 Spectral interferences can be caused by the overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution, or stray light from the line emission of high-concentration elements. Spectral overlap can be corrected after monitoring the interfering element. Each metal must be optimized and the best wavelength chosen. Unresolved overlap requires selection of another wavelength. Background contribution and stray light can be compensated for by performing background correction. An Interference Check Standard and Blank are analyzed at the beginning and end of each day's analyses, and/or every 8 hours, to evaluate the performance of the instrument.

4.3 Changes in viscosity and surface tension can cause significant inaccuracies by interfering with sample flow to the plasma torch, especially in samples containing large amounts of dissolved solids. Physical interferences can be reduced by diluting the sample, by internal standardization with yttrium, or by using standard additions method.

For internal standarization, yttrium is added at a concentration of 1 ppm to all standards, blanks, and samples by the instrument. Sample intensities are adjusted for changes in yttrium response as a function of the instrument program.

4.4 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not substantial with the ICP technique. They can be minimized by careful selection of operating parameters, buffering of samples, matrix matching, and standard addition procedures. Lithium carbonate (200 ppm) is automatically mixed with all standards and samples before analysis for buffering.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 ICP Log Book:

A log book will be maintained for all metals analyses performed on the ICP. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Sample matrix type
- GLA Sample I.D. (one complete for each set)

- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed
- Reviewer's signature and date, where applicable
- All dilution factors

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.

5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value. Appendix A contains information on spiking volumes and concentrations.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 INTERFERENCE CHECKS

The ICP instrument is checked initially and following analytical runs for interferences using an Interference Check Standard and an Interference Check Blank. These are samples containing high concentrations of interfering metals (Al, Ca, Mg, Fe). The Interference Check Standard also contains spiked analytes of interest (Ba, Cd, Cr, Pb, Ag).

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the ICP instrument is calibrated daily, and the calibration checked using a Check Standard. Each individual analyte calibration must have a correlation coefficient, r^2, of at least 0.9950 to be usable. The concentrations of the Check Standard must be within 10% of the expected values.

8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made, or at least annually.

9.0 EQUIPMENT

9.1 ICP Emission Spectrophotometer, TJA 61E TRACE, Liberty 100, or equivalent
9.2 Volumetric flasks, 25-100 mL size.
9.3 Volumetric pipets, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 *Reagent water - ASTM Type II water (DI water). Type I reagent water should be used for the* analysis of earth metals and low level lead.
10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Sulfuric acid - concentrated H_2SO_4 - ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.5 Calibration standards - Standards are prepared in 10% nitric acid. Aliquot 1000 ppm individual analyte standards (purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific) for high standard (level 4) per Table 1 into a 100-mL volumetric flask. Add 10 mL of concentrated HNO_3, dilute to the mark with reagent water, and mix. Prepare the medium standard (level 3) by dilution of the level 4 standard, 10 mL of level 4, 10 mL of concentrated HNO_3, to 100 mL final volume. Prepare the low standard (level 2) by dilution of the level 3 standard, 10 mL of level 3, 10 mL of concentrated HNO_3, to 100 mL final volume. The calibration blank (level 1) is prepared by diluting 10 mL of concentrated HNO_3 to 100 mL final volume.

10.6 Spiking solutions - GLA-SPK-1A and -4B, purchased from Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. As, Se, Zr standard - 1000 ppm.

10.7 Calibration check standard - Add 50 mL of concentrated nitric acid to a 500-mL volumetric flask. Accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.8 Interference check solution - 5000 ppm Al, Ca, Mn, and 2000 ppm Fe, Inorganic Ventures no. CLPP-ICS-A.

10.8 Interference check standard ICS-A - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Dilute to the mark with reagent water and mix.

10.9 Interference check standard ICS-B - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Then, accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.10 Yttrium standard - 10,000 ppm, purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific.

10.11 Lithium carbonate - Li_2CO_3 powder, Fisher no. 5840 or Mallinckrodt no. L119.

10.12 Buffer/internal standard solution - Weigh approximately 10.7 g of Li_2CO_3 and place in a new, clean 2-L fluorinated plastic bottle. Add 1 L of reagent water. Then add 1.0 mL of 10,000 ppm yttrium standard. Carefully add 200 mL of concentrated HNO_3. (Solution will effervesce due to release of carbon dioxide.) Dilute to approximately 2 L with reagent water and mix.

10.13 Rinse solution - 10% nitric acid in reagent water.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: See Table 1 for the analytes for which this method is applicable. See Appendix B for some recommended wave-lengths, estimated instrumental detection limits (IDL), and potential interferences (at the 100 mg/L level).

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

Table 1.
Preparation and Concentrations of Calibration Standard Solutions.

ELEMENT	Volume (mL) of 1000 ppm Standard to Prepare High Standard	High Standard (Level 4) Concentration (ppm)	Medium Standard (Level 3) Concentration (ppm)	Low Standard (Level 2) Concentration (ppm)
Ag	1.0	10.0	1.00	0.100
Al	2.5	25.0	2.50	0.250
As	0.5	5.0	0.50	0.050
B	1.0	10.0	1.00	0.100
Ba	2.5	25.0	2.50	0.250
Be	0.5	5.0	0.50	0.050
Ca	2.5	25.0	2.50	0.250
Cd	0.5	5.0	0.50	0.050
Co	1.0	10.0	1.00	0.100
Cr	1.0	10.0	1.00	0.100
Cu	1.0	10.0	1.00	0.100
Fe	2.5	25.0	2.50	0.250
K	2.5	25.0	2.50	0.250
Mg	2.5	25.0	2.50	0.250
Mn	1.0	10.0	1.00	0.100
Mo	1.0	10.0	1.00	0.100
Na	2.5	25.0	2.50	0.250
Ni	1.0	10.0	1.00	0.100
Pb	0.5	5.0	0.50	0.050
Sb	1.0	10.0	1.00	0.100
Se	0.5	5.0	0.50	0.050
Sn	1.0	10.0	1.00	0.100
Ti	1.0	10.0	1.00	0.100
Tl	1.0	10.0	1.00	0.100
V	1.0	10.0	1.00	0.100
Zn	2.5	25.0	2.50	0.250

Note: See Section 10.5 for complete instructions on calibration standard preparation.

11.2 INTERFERENCE CHECK STANDARD AND BLANK

An Interference Check Standard, containing high amounts of interfering elements and known concentrations of elements of interest, is analyzed at the beginning and the end of each sequence of samples. The interfering elements are the following concentrations: Al, Ca, Mg - 500 ppm, Fe - 200 ppm. The elements of interest are each spiked at 2.0 ppm (exceptTl, which is 4.0 ppm). Recoveries must be within ± 20% of the expected concentrations.

An Interference Check Blank, containing high amounts of interfering elements, is analyzed at the beginning and end of each sequence of samples. This blank contains the same concentrations of interfering elements as the check standard. The Interference Blank is analyzed for Ba, Cd, Cr, Pb, and Ag. The concentrations detected for these elements must not be above the reporting limits.

Internal Standard - Yttrium is added at a concentration of approximately 1.0 ppm to all standards, blanks, and samples by the instrument. The intensity is tracked to ensure proper instrument operation.

11.3 INSTRUMENT CALIBRATION

The ICP is calibrated daily before samples are analyzed. The standard curve includes one blank and three standards (4 levels). The correlation coefficient, r^2, must be at least 0.9950 for each analyte to be run.

The calibration is checked using a Check Standard initially and after every 10 (or fewer) samples. The recovery of the analytes in the Check Standard must be with 10% of expected values. Replicate integrations of the Check Standard must have a %RSD of $\leq$5%. For A2LA required work, the High Level Standard (Level 4)is used as a check of the calibration, and must be within +/-5% of the actual value.

11.4 OPERATION OF THE INSTRUMENT

11.4.1 Power up the instrument and ignite plasma according to the manufacturer's instructions.
11.4.2 Allow instrument to warm up at least 30 minutes.
11.4.3 Perform system profile in accordance with the manufacturer's instructions using an approximately 5 ppm As standard.
11.4.4 Go to analysis section and call up method **6010PM1**.
11.4.5 Calibrate instrument using calibration standards. Each analyte to be used must have a correlation coefficient of at least 0.9950.
11.4.6 Run performance and instrument check samples:

Sample	Criteria
A. ICV (check standard)	±10%
B. ICB (calibration blank)	< reporting limit
C. High standard	±10%
D. ICS-B	±20%
E. ICS-A	< reporting limit (except Al, Ca, Fe, Mg)

11.4.7 If all criteria pass, run samples with a CCV and CCB every 10 (or less) samples. The high standard, ICS-B, and ICS-A need to be re-analyzed at the end of the run, or every 8 hours. Each analytical run must end with a calibration blank and a check standard.

11.4.8 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where: C_x = Concentration of the sample
S_B = The analytical signal for the sample and water solution (corrected for the blank)
V_S = Volume of the standard solution added
C_S = Concentration of the standard solution added
S_A = The analytical signal for the sample and standard solution (corrected for the blank)
V_S = Volume of the sample added to each solution.

Note: V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X , and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

11.5 CALCULATIONS

11.5.1 Results are corrected for any spectral interferences and backgrounds (by the instrument software).

11.5.2 All analyte concentrations are multiplied by the applicable dilution factor (DF) to obtain concentrations for the original samples.

For waters/liquids:

$$\text{concentration (mg/L)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times DF}{\text{initial sample volume (mL)}}$$

For soils/solids/sludges:

$$\text{concentration (mg/kg)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times DF}{\text{initial sample weight (g)}}$$

To report result in dry weight, divide concentration result by decimal percent solids (*e.g.* if %solids is 89%, divide by 0.89).

For paints:

$$\text{concentration (\%)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times DF}{\text{initial sample weight (g)} \times 10{,}000}$$

10,000 is the factor for converting mg/kg (ppm) to percent.

For wipes:

$$\text{amount (mg per wipe)} = \text{instr. result} \times \text{final digestate volume (mL)} \times DF$$

To report in mg per square foot, divide result by area (supplied by client).
To convert to µg, multiply result by 1000.

11.5.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 CLEANING THE PLASMA TORCH

The plasma torch must be cleaned weekly. This is accomplished by soaking the torch in a solution of 1 part concentrated HCl and 3 parts concentrated HNO_3 overnight. The height of the torch will need adjustment when the torch is replaced.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 Method 3120: Metals by Plasma Emission Spectroscopy, Section B (Inductively Coupled Plasma Method); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Method SW-846, 3020B: Inductively Coupled Plasma - Atomic Emission Spectroscopy.
13.4 Great Lakes Analytical Quality Assurance Program.
13.5 Great Lakes Analytical Chemical Hygiene Plan.
13.6 Great Lakes Analytical SOP for Login Department.
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Plan.

APPENDIX A.

STANDARD SPIKING LEVELS AND VOLUMES.

	Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
	GLA-SPK-1A	0.10/100		0.05/50	0.10/50	0.10/50
	GLA-SPK-3B		0.05/50		0.10/50	0.10/50
	GLA-SPK-4B	0.10/100				
	GLA-SPK-5			0.05/50	0.10/50	0.10/50
	GLA-SPK-6					0.10/50
	As/Se Soln.	0.05/50				
	EARTH	0.10/100		0.05/50	0.05/50	

Corresponding Elements and Concentrations (ppm) per matrix

Set	Element	Solid/Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
RCRA	Ag	1.0	0.005		0.01	0.51
	As	0.53	0.015		0.03	0.03
	Ba	1.0		0.50	1.0	1.0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.001	0.001
	Pb	1.0	0.015		0.03	0.03
	Se	0.28	0.015		0.03	0.03
PRIRTY	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1.0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2.03
	Zn	1.0		0.50	1.0	1.0
TAL	Al	1.0		0.5	1.0	1.0
	Co	1.0		0.5	1.0	1.0
	Fe	1.0		0.5	1.0	1.0
	Mn	1.0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0
EARTH	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1.0	1.0	
	Mg	1.0		1.0	1.0	
EXTRA	B	1.0		1.0	2.0	2.0
	Mo	1.0		1.0	2.0	2.0
	Si	1.0		1.0	2.0	2.0
	Sn	1.0		1.0	2.0	2.0
	Ti	1.0		1.0	2.0	2.0

APPENDIX B.

EXAMPLE WAVELENGTHS, ESTIMATED INSTRUMENTAL DETECTION LIMITS (IDL), AND POTENTIAL INTERFERENCES AT THE 100 mg/L LEVEL.

Element	Wavelength (nm)	IDL (µg/L)	Interferent(s) *
Aluminum (Al)	308.215	30	Mn 0.2, V 1.4
Antimony (Sb)	206.833	21	Al 0.5, Cr 2.9, Fe 0.1, Ti 0.3, V 0.5
Arsenic (As)	193.696	35	Al 1.3, Cr 0.4, V 1.1
Barium (Ba)	455.403	0.9	
Beryllium (Be)	313.042	0.2	Ti 0.04, V 0.05
Boron (B)	249.678†	3.8	
Cadmium (Cd)	226.502	2.3	Fe 0.03, Ni 0.02
Calcium (Ca)	317.933	6.7	Cr 0.1, Mn 0.04, Ti 0.03, V 0.03
Chromium (Cr)	267.716	4.7	Mn 0.04, V 0.04
Cobalt (Co)	228.616	4.7	Cr 0.03, Fe 0.01, Ni 0.03, Ti 0.15
Copper (Cu)	324.754	3.6	Ti 0.05, V 0.02
Iron (Fe)	259.940	4.1	Mn 0.1
Lead (Pb)	220.353	28	Al 0.2
Lithium (Li)	670.784	2.8	
Magnesium (Mg)	279.079	20	Cr 0.1, Fe 0.1, Mn 0.3, Ti 0.1, V 0.1
Manganese (Mn)	257.610	0.9	Al 0.01, Cr 0.01
Mercury (Hg)	194.227†	17	
Molybdenum (Mo)	202.030	5.3	Al 0.05, Fe 0.03
Nickel (Ni)	231.604†	10	
Phosphorus (P)	213.618	51	
Potassium (K)	766.491	‡	
Selenium (Se)	196.026	50	Al 0.2, Fe 0.1
Silica (SiO_2)	251.611	17	
Silver (Ag)	328.068	4.7	
Sodium (Na)	588.995	19	Ti 0.08
Strontium (Sr)	407.771	0.3	
Thallium (Tl)	190.864	27	Al 0.3
Tin (Sn)	189.9890†	17	
Titanium (Ti)	334.941	5.0	
Vanadium (V)	292.402	5.0	Cr 0.05, Fe 0.01, Ti 0.02
Zinc (Zn)	213.856†	1.2	Cu 0.1, Ni 0.3

† second order.
‡ highly dependent on operating conditions and plasma position.
* analyte concentration equivalents.

Sequoia Analytical

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METALS
METHOD EXCEPTION (37)

Date Effective: 12/1/98 Supersedes: 1/1/92
Method No.: EPA 6010A
Method Title: Inductively Coupled Plasma Atomic Emission Spectroscopy

The above method is currently being used with the following exceptions:

The following have been added to the analyte list:

Germanium	CAS No.:	7440-56-4
Tantalum	CAS No.:	7440-25-7

THERE ARE NO ADDITIONAL EXCEPTIONS TO THIS METHOD.

Approved by: [signature] Date: 6-1-98

NOTE: The above information reflects current modifications to the method.

METHOD #: 6010A (SW-846 Update I, July 1992)

TITLE: Inductively Coupled Plasma-Atomic Emission Spectroscopy

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide estimated detection limits for clean aqueous samples using pneumatic nebulization. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

ANALYTE:	CAS #
Aluminum Al	7440-36-0
Antimony Sb	7440-36-0
Arsenic As	7440-38-2
Barium Ba	7440-39-3
Beryllium Be	7440-41-7
Cadmium Cd	7440-43-9
Calcium Ca	7440-70-2
Chromium Cr	7440-43-9
Cobalt Co	7440-48-4
Copper Cu	7440-50-8
Iron Fe	7439-89-6
Lead Pb	7439-92-1
Lithium Li	7439-93-2
Magnesium Mg	7439-95-4
Manganese Mn	7439-96-5
Molybdenum Mo	7439-98-7
Nickel Ni	7440-02-0
Phosphorous P	7723-14-0
Potassium K	7440-09-7

Selenium Se	7782-49-2
Silver Ag	7440-22-4
Sodium Na	7440-23-5
Strontium Sr	7440-24-6
Thallium Tl	7440-28-0
Vanadium V	7440-62-2
Zinc Zn	7440-66-6

INSTRUMENTATION: ICP

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Methods 3005-3050). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 8.5.

TABLE 1. RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection	Wavelength(a)(nm)	Estimated Element Limit(b) (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7

Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
ganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

(a) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.

(b) The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

(c) Highly dependent on operating conditions and plasma position.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuum or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternative wavelength. Background contribution and stray light can usually be compensated for by a correction adjacent to the analyte line.

Users of all ICP instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Recommended wavelengths are listed in Table 1 and potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately

0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc. The user should be aware of the possibility of interferences other than those specified in Table 2 and that analysts should be aware of these interferences when conducting analyses.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

TABLE 2. ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

		Interferent(a,b)									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

(a) Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L
Ca - 1000 mg/L
Cr - 200 mg/L
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L
Mn - 200 mg/L
Tl - 200 mg/L
V - 200 mg/L

(b) The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Changing the nebulizer and removing salt buildup at the tip of the torch sample injector can be used as an additional measure to control salt buildup. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator compliant with FCC regulations.

4.1.3 Argon gas supply - Welding grade or better.

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

4.3 Class A volumetric flasks

4.4 Class A volumetric pipets

4.5 Analytical balance- capable of accurate measurement to 4 significant figures.

5.0 REAGENTS

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American

Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.
5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriate beaker.
5.1.3 Nitric acid (conc), HNO3.
5.1.4 Nitric acid (1:1), HNO3. Add 500 mL concentrated HNO3 to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultrahigh purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105-C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 ug Al: Dissolve 1.0 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
5.3.2 Antimony solution, stock, 1 mL = 1000 ug Sb: Dissolve 2.70 g K(SbO)C4H4O6 (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.
5.3.3 Arsenic solution, stock, 1 mL = 1000 ug As: Dissolve 1.30 g of As2O3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.
5.3.4 Barium solution, stock, 1 mL = 1000 ug Ba: Dissolve 1.50 g BaCl2 (mole fraction Ba = 0.6595), dried at 250-C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.
5.3.5 Beryllium solution, stock, 1 mL = 1000 ug Be: Do not dry.

Dissolve 19.5 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Cadmium solution, stock, 1 mL = 1000 ug Cd: Dissolve 1.10 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.7 Calcium solution, stock, 1 mL = 1000 ug Ca: Suspend 2.50 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180-C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Chromium solution, stock, 1 mL = 1000 ug Cr: Dissolve 1.90 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Cobalt solution, stock, 1 mL = 1000 ug Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO . Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Copper solution, stock, 1 mL = 1000 ug Cu: Dissolve 1.30 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Iron solution, stock, 1 mL = 1000 ug Fe: Dissolve 1.40 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Lead solution, stock, 1 mL = 1000 ug Pb: Dissolve 1.60 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lithium solution, stock, 1 mL = 1000 ug Li: Dissolve 5.324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Magnesium solution, stock, 1 mL = 1000 ug Mg: Dissolve 1.70 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Manganese solution, stock, 1 mL = 1000 ug Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Molybdenum solution, stock, 1 mL = 1000 ug Mo: Dissolve 2.00 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Nickel solution, stock, 1 mL = 1000 ug Ni: Dissolve 1.00 g of

nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.18 Phosphate solution, stock, 1 mL = 1000 ug P: Dissolve 4.393 g anhydrous KH2PO4 (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Potassium solution, stock, 1 mL = 1000 ug K: Dissolve 1.90 g KCl (mole fraction K = 0.5244) dried at 110-C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Selenium solution, stock, 1 mL = 1000 ug Se: Do not dry. Dissolve 1.70 g H2SeO3 (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Silver solution, stock, 1 mL = 1000 ug Ag: Dissolve 1.60 g AgNO3 (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Sodium solution, stock, 1 mL = 1000 ug Na: Dissolve 2.50 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Strontium solution, stock, 1 mL = 1000 ug Sr: Dissolve 2.415 g of strontium nitrate (Sr(NO3)2) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.24 Thallium solution, stock, 1 mL = 1000 ug Tl: Dissolve 1.30 g TlNO3 (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Vanadium solution, stock, 1 mL = 1000 ug V: Dissolve 2.30 g NH403 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Zinc solution, stock, 1 mL = 1000 ug Zn: Dissolve 1.20 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO3. Add 10.0 mL concentrated HNO3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Matrix match with the appropriate acids and dilute to 100 mL with water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Step 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of

inter-element spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li,& Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The method blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.1.1 for use). The instrument check standard should be prepared from a source independent from that used in the calibration standards.

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes, Steps 3.1 through 3.3.

7.0 PROCEDURE

1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

7.2 Set up the instrument with proper operating parameters established in Step 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and three standards.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 minute (Step 5.5.1) before the analysis of each sample (see Note to Step 7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for additional quality control procedures.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples.

8.4 Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Refer to Chapter One for a more detailed description of an analytical batch.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the

instrumental detection limit after dilution), an analysis of a 1:4-dilution should agree within +/- 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

8.6.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.1.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

8.6.1.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.2 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution (Step 5.7). Results should be within +/- 20% of the true value obtained in Step 8.6.1.1.

8.6.3 Spiked replicate samples are to be analyzed at a frequency of 5% or per analytical batch, whichever is more frequent.

8.6.3.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

where:

RPD = relative percent difference.
D1 = first sample value.
D2 = second sample value (replicate).

(A control limit of +/- 20% RPD shall be used for sample values greater than ten times the instrument detection limit.)

8.6.3.2 The spiked replicate sample recovery is to be within +/- 20% of the actual value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9 +/- 2%. The mean percent recovery of spiked elements for all wastes was 93 +/- 6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

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TABLE 4. ICP PRECISION AND ACCURACY DATA(a)

	Sample No. 1			Sample No. 2			Sample No. 3		
Element	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD(b) (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
(	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13

Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

(a) Not all elements were analyzed by all laboratories.
(b) SD = standard deviation.
(c) Results for Se are from two laboratories.

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GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ORGANIC EXTRACTION AND SAMPLE PREPARATION FOR

SEMIVOLATILE DETERMINATIVE METHODS

GLA 3500 BG

Revision 1.1

Approved By:

Department Manager: _____ Date: 5-28-99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the selection and use of procedures for the extraction, dilution, and cleanup of samples for analysis by semivolatile determinative methods. This SOP is an interpretation of several EPA extraction methods, including 3500B, 3510C, 3550B, and 3580A, and cleanup methods 3620B, 3640A, 3660B, and 3665A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

2.1 Samples of known volume or weight are extracted with solvent, or diluted with solvent, in preparation for analysis. One of the following methods is used depending upon sample type:

- Aqueous samples are extracted using separatory funnel liquid-liquid extraction (method 3510C). For example, 1000 mL of sample is extracted using three 60 mL portions of methylene chloride (section 11.1).
- Soil/sediment samples are extracted using ultrasonic extraction (method 3550B). For example, 30 g of sample is extracted using three 100 mL portions of methylene chloride (sections 11.3 and 11.4).
- Samples for herbicide analysis are extracted and derivatized using diazomethane (method 8151, sections 11.2 and 11.5).
- Non-aqueous solvent soluble samples are diluted (method 3580A). For example, 1-2 g of sample is mixed with 10 mL of methylene chloride (section 11.6).

2.2 Some samples may be required to be placed through a cleanup procedure to eliminate interferences. Sample cleanup procedures are:

- Samples for PCB analysis are treated with sulfuric acid (method 3665A) to remove interferences (section 12.1). Sulfur cleanup is required following the sulfuric acid cleanup procedure.
- Soluble sulfur can be removed using copper (method 3660B, section 12.2).
- Florisil (magnesium silicate) may be used to separate analytes from interfering compounds (method 3620B, section 12.3).
- Cleanup using gel permeation chromatography (GPC, method 3640A) may be used to separate molecules of different sizes (section 12.4)

2.3 The resultant extracts are dried using anhydrous sodium sulfate and concentrated using Kuderna-Danish (K-D) apparatus, or in an automated concentration device. The extracts are analyzed, for example, per one of EPA methods 8015, 8081, 8082, 8151, 8270, or 8310.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents (use nitrile gloves to avoid contamination with plasticizers).

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples (use nitrile gloves to avoid contamination with plasticizers). Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, are not used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 Materials causing interferences may be coextracted from a sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

5.0 RECORD KEEPING

5.1 Extraction logbooks contain records of analytical batches.

5.2 Analytical batch records must contain the following information:
- 5.2.1 Sample volume or weight.
- 5.2.2 Client name or sample number.

5.2.3 Great Lakes sample number.
5.2.4 Extraction method.
5.2.5 Analytical method.
5.2.6 Date(s) extracted and concentrated.
5.2.7 Lab batch ID number.
5.2.8 Extraction or dilution solvent, and lot number.
5.2.9 Final solvent (if different), and lot number.
5.2.10 Initials of analyst(s).
5.2.11 Lab lot ID# of spiking solution(s).
5.2.12 Final volume of extract.
5.2.13 Any "cleanup" methods used.

An example of a logbook page for an analytical batch record is attached to this SOP (see Attachment 1).

5.3 All unused portions of logbook pages must be z'ed out.

6.0 QUALITY CONTROL

6.1 For quality control, each water extraction batch contains a method blank (MB), and laboratory control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). An analytical batch contains no more than 20 samples. Deionized water is used for water method blanks and spikes.

6.2 Each soil extraction batch (not more than 20 samples) contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). Clean sand is used for soil method blanks (MB) and blank spikes (LCS). Soil samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates. The extractionists can override this if insufficient sample is available, or if chosen sample is extremely dirty.

6.3 Surrogate compounds are added to all samples, blanks, and spikes in an analytical batch.

6.4 Descriptions of the standards used for spiking and as surrogates are given in the individual analytical method SOPs. For example, method 8151 (Herbicides) uses a spiking standard containing 0.1 to 1.3 mg/mL of herbicide compounds and a surrogate of 100 µg/mL dichorophenylacetic acid (DCAA or DCPA).

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 LIMS extraction batching procedure:
7.2.1 At the LIMS main menu screen, select B (batching), new batch.
7.2.2 At the Queue prompt, type in "EXTR" and press F8.
7.2.3 Highlight the test wanted from the list of available methods and double-click.
7.2.4 Deselect any samples by clicking on the corresponding √ (check mark).
7.2.5 Click on "Build Batch", then "Add QC". Press "Save".
7.2.6 At name prompt, enter initials of extractionist.
7.2.7 When the batch list appears on screen, highlight "Please Select A Printer", press "List" and choose the "SVOC LIMS Printer".
7.2.8 Select "OK" at all prompts.

8.0 METHOD VALIDATION

Each new extractionist will perform a series of extractions to establish the ability to generate acceptable precision and accuracy. For each analytical method:

8.1 Four 1000 mL blank water samples (method validation for water analysis), or four 30 g blank sand samples (method validation for soil analysis), are extracted and concentrated, each spiked with 1.0 mL of the QC spiking solution (see method 3500B, Section 8.2.4).
8.2 The extracts will be analyzed and the average percent recovery and the standard deviation of the percent recoveries for each component of the spikes will be calculated.
8.3 Acceptance criteria are found in the appropriate determinative method.
8.4 Documentation of these analyses will be maintained in the employee's training file.

9.0 EQUIPMENT

NOTE: The exact equipment necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

9.1 Graduated cylinders - 1000-mL, for measuring volume of aqueous samples.
9.2 Separatory funnels - 2-L and 125-mL, with PTFE stopcocks and caps.
9.3 pH indicator paper - range to cover pH 0 to 13.
9.4 Solvent dispensers, for 30 to 100 mL (two 50-mL dispenses may be used for 100 mL).
9.5 Squirt bottles for solvents.
9.6 Benchtop shaker, for separatory funnels.
9.7 Laboratory timer, clock, or wristwatch.
9.8 Erlenmeyer flasks - 500 and 125-mL, for collecting sample extracts.
9.9 Filter funnels - 75 mm, fluted bowl, short stem.
9.10 Filter paper - Whatman No. 41 (or equivalent) to fit filter funnels.
9.11 Boiling chips, PTFE (Teflon).
9.12 Spatula, stainless steel or PTFE.
9.13 Glass Pasteur pipets.
9.14 Kuderna-Danish (K-D) apparatus, each consisting of:
- Concentrator tube - 10 mL, graduated.
- Evaporator flask - 500 mL.
- Snyder column - three-ball macro.
- Clamps - for securing glassware at ground-glass joints.

9.15 Water bath - heated, with concentric ring cover, temperature setting on "High" for approximately 95°C.
9.16 Oven, capable of maintaining 400-500°C.
9.17 Syringes, glass - 2.5 mL, 1.0 mL, and 100 µL.
9.18 Syringe filters - 0.2 µm, 13 mm, Acrodisk, Fisher no. SJFGO13NS.
9.19 Nitrogen blowdown apparatus - Organomation N-EVAP, or equivalent, connected to nitrogen gas source, temperature setting at about "5" for approximately 50°C bath temperature.
9.20 Balance - top-loading, capable of accurately weighing to the nearest 0.01 g.
9.21 Beaker - 250 mL, for sonicating samples.
9.22 Ultrasonic disrupter - with minimum power of 300 watts, equipped with dual ¾" horns, Heat Systems XL, or equivalent.
9.23 Sonabox - used to decrease cavitation sound from disrupter.
9.24 Ultrasonic water bath - Branson 8210, or equivalent.
9.25 Automatic evaporative concentrator - Zymark Turbo Vap II.
9.26 Concentrator tubes - Zymark, 200 mL, 1.0 mL tip.
9.27 Glass chromatography column, 20 mm diameter, approximately 30 cm length.
9.28 HPLC for GPC cleanup, consisting of:
- Solvent pump - capable of delivering 5 mL/min.
- Sample injector - with 0.5 mL sample loop.

- GPC Cleanup columns - Waters Envirogel, 19 × 150 mm and 19 × 300 mm.
- UV absorbance detector - with mercury lamp for 254 nm.
- Flow transfer valve - for eluent to waste or collect.
- Integrator or chart recorder.
- Solvent supply and waste containers.

10.0 STANDARDS AND REAGENTS

NOTE: The exact standards and reagents necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

10.1 Reagent water - organic-free deionized (DI water), Fisher no. W5.
10.2 Acetone - pesticide grade or equivalent, Fisher no. A929.
10.3 Acetonitrile - pesticide grade or equivalent, Fisher no. A21.
10.4 Diethyl ether - pesticide grade or equivalent, Fisher no. E197.
10.5 Methanol - pesticide grade or equivalent, Fisher no. A453.
10.6 Hexane - pesticide grade or equivalent, Fisher no. H303.
10.7 Methylene chloride ($MeCl_2$) - pesticide grade or equivalent, Fisher no. D151.
10.8 Acetone/methylene chloride solution (1:1 v/v) - Mix 500 mL of acetone with 500 mL of methylene chloride in a 1-L bottle.
10.9 6%, 15%, and 50% Diethyl ether in hexane solution (v/v) - Mix proportionate volumes of diethyl ether and hexane in a 1-L bottle. For example, 60 mL ether and 940 mL hexane for 6%, 150 and 850 for 15%, or 500 and 500 for 50% (v/v) solutions.
10.10 Sodium hydroxide - pellets, NF/FCC grade, Fisher no. S320. **CAUTION:** Sodium hydroxide is corrosive.
10.11 Sodium hydroxide solution (10 N) - Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.
10.12 Sulfuric acid - concentrated (18 M), ACS grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.13 50% Sulfuric acid solution (1:1 v/v) - Carefully pour 50 mL of concentrated sulfuric acid into 50 mL of water. **CAUTION:** Reaction is exothermic.
10.14 Hydrochloric acid - concentrated, ACS grade or equivalent, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.15 Sodium sulfate - granular, anhydrous, Fisher no. S415. Purify by heating at 400-500°C for at least 4 hours.
10.16 Acidified sodium sulfate for method 8151 - Slurry 100 g of purified sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH. The pH must be less than 4. Store the remaining solid at 130°C.
10.17 Sand - washed sea sand, Fisher no. S25. Purify by heating at 400-500°C for at least 4 hours.
10.18 Sodium chloride - analytical reagent grade, Mallinckrodt no. 7581.
10.19 Copper - granular or powder, copper should be reactive, as evidenced by a bright shiny appearance, JT Baker no. 1720-01.
10.20 Florisil - granular, 60-100 mesh, Fisher F100. Prepared by heating at 400-500°C for at least 4 hours.
10.21 GPC Calibration Standards - consisting of corn oil, phthalate, methoxychlor, perulene, and sulfur; Vitron Scientific no. CLP-340.
10.22 Diazald, N-methyl-N-nitroso-p-toluenesulfonamide - high purity grade, Aldrich no. D2,800-0.
10.23 Ethoxyethoxy ethanol (Carbitol, diethylene glycol monoethyl ether), reagent grade, Aldrich no. E455-0.
10.24 Potassium hydroxide - pellets, NF/FCC grade, Mallinckrodt no. 6976. **CAUTION:** Sodium hydroxide is caustic.
10.25 Potassium hydroxide solution (37% w/v). Dissolve 37 g of potassium hydroxide (KOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.

10.26 Potassium hydroxide solution (12% w/v). Dilute one volume of 37% KOH solution with two volumes of water. For example, dilute 30 mL KOH solution with 60 mL of water.

11.0 EXTRACTION PROCEDURES

Refer to the summary of extraction procedures, Attachment 2 of this SOP.

11.1 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (METHOD 3510C)

11.1.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

NOTE: If high analyte concentrations are anticipated, a smaller sample volume may be measured and diluted to 1000 mL with water. Record the volume used for later calculations of dilution factor and analyte concentrations.

11.1.2 Using a 1.0-mL syringe, add 1.0 mL (50 µL for 8015 methods) of the appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water.

11.1.3 For methods 8081, 8082, and 8270, check the pH of the sample(s) with pH paper. If necessary, adjust the pH using 50% (1:1 v/v) sulfuric acid solution or 10 N sodium hydroxide, to the following pH values:

- Method 8081 - between 5 and 9 (inclusive).
- Method 8082 - between 5 and 9 (inclusive).
- Method 8270 - first set of extractions ≤2, second set of extractions ≥11.

Samples for methods 8015 and 8310 do not require checking or adjustment.

11.1.4 For each sample, use 60 mL of methylene chloride (60 mL of hexane for method 8015D) to rinse the sample bottle and the graduated cylinder. Transfer to the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.1.5 Allow the organic layer (*i.e.* the bottom layer if methylene chloride, top layer if hexane) to separate from the water phase. The layers should be visually separate. Collect the solvent extract in a 500-mL Erlenmeyer flask.

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

11.1.6 Repeat the extraction two more times using fresh 60 mL portions of solvent. Combine the three solvent extracts in the Erlenmeyer flask. Combine all extracts in the Erlenmeyer flask.

NOTE: If extracting sample for method 8270, perform three extractions. Then adjust the pH of the sample to ≥11 using 10 N sodium hydroxide and re-extract the sample three more times.

11.1.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with about 15-20 mLs of solvent. Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column.

11.1.8 Place the K-D apparatus on the hot water bath so the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.1.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, add acetonitrile to a final volume of 10 mL. For methods 8015, 8081, 8082, and 8070, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

11.1.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.1.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.2 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

11.2.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

11.2.2 Using a 1.0-mL syringe, add 1.0 mL of appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water. Add 250 g of sodium chloride to each sample and shake to dissolve.

11.2.3 Add approximately 10 mL of cold 50% sulfuric acid to each sample. Check the pH of the sample(s) with pH paper. If necessary, adjust the pH using additional 50% sulfuric acid to ≤2.

11.2.4 For each sample, rinse the sample bottle and graduated cylinder with 120 mL of diethyl ether, and place in the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.2.5 Allow the ether (top) layer to separate from the water phase. The layers should be visually separate. Drain the water (lower) layer into a clean beaker or Erlenmeyer flask. Collect the ether extract in an Erlenmeyer flask containing some acidified anhydrous sodium sulfate.

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

11.2.6 Pour the aqueous phase back into the separatory funnel. Repeat the extraction two more times using fresh 60 mL portions of ether. Combine all extracts in the Erlenmeyer flask.

11.2.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding additional acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained (let sit 1½ to 2 hours). Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with 20-25 mL of ether, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with 15-20 mLs of ether.

11.2.8 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.2.9 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool. For each extract, add 0.5 of methanol, 1 mL of hexane, and bring to 4 mL volume with ether.

11.2.10 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS.

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11.2.11 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11.2.12 Dilute the extracts to final volume of 10 mL with hexane.

11.2.13 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.3 ULTRASONIC EXTRACTION (METHOD 3550B, except for 8015 WDRO)

11.3.1 Weigh approximately 30 g (*i.e.* 25-35 g) of sample into 500-mL beaker and record the weight to the nearest 0.1 g. Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand.

11.3.2 For methods 8081, 8082, 8270, and 8310, add 1.0 mL of the surrogate standard solution to each sample, blank and QC samples. For method 8015 (TPHD), add 50 µL of the surrogate standard solution to each sample, blank and QC samples. Add 1.0 mL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate.

11.3.3 Add 100 mL of extraction solvent (methylene chloride for methods 8270, 8310 and 8015 TPHD; 1:1 (v/v) acetone/methylene chloride for methods 8081 and 8082) to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.

11.3.4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent, but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous), and percent-duty cycle knob set at 50% (*i.e.* energy on 50% of the time and off 50% of the time).

11.3.5 Decant the extract and filter it through a filter funnel containing a folded filter paper and anhydrous sodium sulfate into a Kuderna-Danish (K-D) apparatus.

11.3.6 Repeat the extraction two more times with two additional 100 mL portions of solvent. After each extraction, filter the extract through the sodium sulfate filter into the K-D apparatus. If the sodium sulfate appears completely hydrated, replace the filter paper and use fresh sodium sulfate. Rinse the filter funnel with about 15-20 mLs of solvent.

11.3.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

11.3.8 When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.3.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, bring extract to a final volume of 10 mL with acetonitrile. For methods 8015, 8081, 8082, and 8270, use the nitrogen blow-down apparatus to reduce extract volume to 1 mL.

11.3.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.3.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.3.12 Each soil sample extracted must also have the % dry weight determined. Refer to SOP GLA160BG.

11.4 WDRO SOIL SAMPLE PRESERVATION AND ULTRASONIC EXTRACTION (8015 WDRO)

NOTE: Hexane must be added to soil containers within 72 hours of collection.

11.4.1 Weigh the sample jar and subtract the empty weight to determine the actual soil weight. Record the sample weight in the soil preservation logbook. If the sample weight in a 2 oz jar is >35 grams, or in a 4 oz jar is >70 grams, indicate this in the logbook.

11.4.2 Add hexane to the sample jar in a 1:1 ratio of mL hexane to grams of sample. (If the sample weight is less than 25 g, then add 25 mL hexane.) Add an amount of anhydrous sodium sulfate equal to the sample weight to the sample jar. Spike the sample with 50 µL of WDRO surrogate standard solution. Cap and mix by shaking briefly. Store sample jars in the sample refrigerator until ready for extraction (Section 11.3.3 and following).

11.4.3 WDRO soil sample jars are placed in an water bath and sonicated for 20 minutes. After sonication, the sample extract is filtered through a filter funnel containing a folded piece of filter paper and sodium sulfate into a 200-mL Zymark concentrator tube.

11.4.4 Approximately 30 mL of fresh hexane is added to the sample jar. The jar is capped tightly, placed again in the ultrasonic water bath and sonicated for 20 minutes. After sonication, the contents of the jar are filtered through the filter funnel into the same concentrator tube as the first filtrate. The sample jar is rinsed with about 20-25 mLs of hexane, which is then filtered through the filter funnel.

11.4.5 The concentrator tubes containing the sample extracts are placed into the Turbo Vap II automatic evaporative concentrator, and the evaporation cycle started. The Turbo Vap II automatically concentrates the extract to 1 mL, and then audibly signals that the cycle is complete.

11.4.6 Using a glass Pasteur pipet, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.5 ULTRASONIC EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

11.5.1 For each sample, weigh approximately 30 g (*i.e.* 25-35 g) of sample into a 500-mL beaker and record the weight to the nearest 0.1 g. (For wipe samples, weigh the entire wipe.) Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand. Adjust the pH of sample to ≤2 with concentrated hydrochloric acid.

11.5.2 Add 100 µL of the surrogate standard solution to each sample, blank and QC samples. Add 100 µL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate.

11.5.3 Add 100 mL of methylene chloride to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.

11.5.4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent (approximately 0.5 inches), but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous), and percent-duty cycle knob set at 50% (*i.e.* energy on 50% of the time and off 50% of the time).

11.5.5 Place the extract in an Erlenmeyer flask. Repeat the extraction two more times with fresh 100 mL portions of methylene chloride. Combine extracts.

11.5.6 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Then pass the extract through a filter funnel, containing a folded filter paper containing some acidified anhydrous sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mL of solvent.

11.5.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

11.5.8 When the volume of extract reaches approximately 5 mL, remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.5.9 For each sample, place the concentrated extract into a 125-mL separatory funnel. Extract using 15 mL of 12% potassium hydroxide. Shake vigorously for 2 minutes.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.5.10 Drain the organic (lower) layer into a clean beaker. Drain the aqueous layer into an Erlenmeyer flask. Pour the organic layer back into the separatory funnel. Extract twice more using fresh 15 mL portions of 12% potassium hydroxide. Combine aqueous extracts.

11.5.11 Adjust the pH of the aqueous extract to ≤2 with cold 50% sulfuric acid. Place in a clean 125-mL separatory funnel and extract using 40 mL of diethyl ether. Shake vigorously for 2 minutes.

CAUTION: Addition of sulfuric acid to the sample may cause an exothermic reaction. Vent the separatory funnel to release pressure.

11.5.12 Drain the aqueous (lower) layer into a clean beaker. Drain the ether extract layer into an Erlenmeyer flask. Pour the aqueous layer back into the separatory funnel. Extract twice more using fresh 20 mL portions of ether. Combine ether extracts.

11.5.13 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mLs of solvent.

11.5.14 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of ether to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

11.5.15 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool.

11.5.16 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS.

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11.5.17 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11.5.18 Dilute the extracts to final volume of 10 mL with hexane.

11.5.19 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.6 WASTE DILUTION (METHOD 3580A)

11.6.1 Depending on the determinative method requested for the waste dilution sample, a small amount (1-2 g) of sample is mixed in a beaker with approximately 10 mLs of the appropriate solvent. If the sample dissolves in the solvent, the sample can then proceed through the waste dilution procedure (11.4.2). If the sample does not dissolve in the appropriate solvent, then the sample must be extracted as either a water or a soil, depending upon the nature of the sample.

11.6.2 Weigh approximately 1 g (0.9 to 1.1 g) of sample into a 250-mL beaker, add 1 mL of the waste dilution surrogate spike solution, and bring to 10 mL final volume with the solvent appropriate for the determinative method. Mix until the sample is fully dissolved. The method blank is 1 mL of the waste dilution surrogate spike solution and 9 mL of solvent mixed in a 250-mL beaker. The blank spike and duplicate are each made by mixing 1 mL of the appropriate spiking solution, 1 mL of the waste dilution surrogate spiking solution, and 8 mL of solvent in 250-mL beakers.

11.6.3 If the sample solution requires cleanup, see the appropriate cleanup procedure(s), Section 12.0.

11.6.4 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

12.0 CLEANUP PROCEDURES

12.1 SULFURIC ACID CLEANUP (METHOD 3665A)

12.1.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's only, and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This method uses sulfuric acid for the removal of these substances. The method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

12.1.2 The cleanup procedure is performed in a 4-mL clear glass vial with a Teflon-lined screw cap. One mL of hexane extract and and 1 mL of concentrated sulfuric acid are added to the vial, the vial is tightly capped, and then vigorously shaken by hand or on a mechanical shaker for 5 minutes. The solution is then allowed to separate into acid (lower) and hexane (upper) layers. Complete separation of the layers may take between 5 minutes and several hours. Separation can sometimes be expedited by centrifuging the solution. After the layers completely separate, transfer the hexane layer to a new autosampler vial for sulfur cleanup, and proceed with Section 12.2.

12.2 SULFUR CLEANUP (METHOD 3660B)

12.2.1 This cleanup procedure is applicable to sample extracts that are suspected to contain dissolved sulfur, or extracts that have been analyzed and have been shown to contain dissolved sulfur. This procedure uses copper powder for the removal of dissolved sulfur.

12.2.2 The cleanup procedure is performed directly in the sample extract autosampler vial. Granular copper (20-30 mesh, about 2 g) is added to the 1 mL of extract in the vial to fill about ¼ of the vial volume. The vial is capped and shaken vigorously by hand or on a mechanical shaker for 5 minutes. If the shiny surface of the granular copper turns completely black the extract may still contain dissolved sulfur, in which case the extract should be transferred to a new vial, and the procedure repeated with a fresh portion of copper. If the copper has not turned completely black, transfer the cleaned extract to a new labeled autosampler vial for analysis, through a syringe filter attached to a 1-mL Luer-Lok syringe.

12.3 FLORISIL CLEANUP (METHOD 3620B)

CAUTION: Notify the Inorganics Department that ether will be in use.

12.3.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's and/or organochlorine pesticides, and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This procedure is intended only for the cleanup of samples, and not for fractionation. Standardized Florisil must be used for fractionation.

12.3.2 Add approximately 20 g of dried Florisil to a 20 mm glass chromatography column. Settle the Florisil by gently tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep.

12.3.3 Pre-elute the column with 60 mL of hexane and discard the eluate. Drain the column until the sodium sulfate layer is nearly exposed (*i.e.* solvent drained down to the top of the layer). Quantitatively transfer the sample extract onto the column, completing the transfer using two 1-2 mL rinses with hexane.

12.3.4 Place a 500-mL K-D flask equipped with a clean 10-mL concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% diethyl ether in hexane (v/v), using a drip rate of about 5 mL/minute; followed by 200 mL of 15% ether/hexane, and 200 mL of 50% ether/hexane.

NOTE: If the sample is to be analyzed only for PCB's, then only elute with 200 mL of 50% diethyl ether in hexane.

12.3.5 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

12.3.6 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

12.3.7 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

12.4 GEL PERMEATION CLEANUP (METHOD 3640A)

12.4.1 Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels to separate molecules of different sizes. For example, GPC cleanup can be used to remove lipids, polymers, copolymers, proteins, and natural resins from samples.

12.4.2 Set the flow rate to 5 mL/min of methylene chloride. Switch the flow transfer valve for the eluent to flow to waste.

12.4.3 For each sample, prepare a Kuderna-Danish (K-D) apparatus for collection of sample eluent.

12.4.4 Retention times of the components of the GPC calibration standards must be checked at least once per week when running this cleanup procedure. Flush and load the sample loop using 1 mL of standard solution. Inject and start the chart recording. Determine and record the retention times for each component. Note elution times for the end of the phthalate peak and the beginning of the sulfur peak.

12.4.5 For cleanup of samples, flush and load the sample loop using 1 mL of sample. Inject and start the chart recording. Immediately after the elution time of phthalate, switch the flow transfer valve for eluent to the outlet line leading to the K-D. Just before the elution time of sulfur, switch the valve to transfer flow to waste. Allow sufficient time for sulfur compounds to elute before injection of another sample.

12.4.6 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8081 and 8082), do not remove the K-D apparatus, pour 50 mL of hexane into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

12.4.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 0.5 mL.

12.4.8 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

13.0 MAINTENANCE AND TROUBLESHOOTING

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation.

14.0 REFERENCES

14.1 EPA Method 3500B: Organic Extraction and Sample Preparation.
14.2 EPA Method 3510C: Separatory Funnel Liquid-Liquid Extraction.
14.3 EPA Method 3550B: Ultrasonic Extraction.
14.4 EPA Method 3580A: Waste Dilution.
14.5 EPA Method 3620B: Florisil Cleanup.
14.6 EPA Method 3660B: Sulfur Cleanup.
14.7 EPA Method 3665A: Sulfuric Acid/Permanganate Cleanup.
14.8 EPA Method 8015B: Nonhalogenated Organics Using GC/FID.
14.9 EPA Method 8081A: Organochlorine Pesticides by Gas Chromatography.
14.10 EPA Method 8082: Polychlorinated Biphenyls by Gas Chromatography.
14.11 EPA Method 8270C: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).
14.12 EPA Method 8310: Polynuclear Aromatic Hydrocarbons.
14.13 EPA Method 8151: Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization.
14.14 Modified DRO – Method for Determining Diesel Range Organics (Wisconsin DNR).
14.15 Great Lakes Analytical Quality Assurance Program manual.
14.16 Great Lakes Analytical Chemical Hygiene Plan.
14.17 Great Lakes Analytical SOP for Login Department.
14.18 Great Lakes Analytical SOP for Hazardous Sample Management.
14.19 Gel Permeation Chromatography Cleanup System, Operator's Guide, Waters Chromatography Division, Millipore Corporation.

15.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

ATTACHMENT 1

SEMIVOLATILES WATER/SOIL EXTRACTION LOG **Page x of 100**

Extraction Method _____ Analytical Method _____

Date Extracted _____ by _____ Sample Matrix _____

Date Concentrated _____ by _____ Date Completed _____ by _____

Extraction Solvent _____ Lot _____ Final Solvent _____ Lot _____ by ____

Surrogate Spike Solution No. _____

Matrix Spike Solution No. _____ **BATCH No.** _____

	Client or ID	Sample No.	Sample Size (mL/g)	Surrogate Volume (mL)	Spike Volume (mL)	pH Adjustment	Solvent Exchange	Final Volume (mL)	Comments/ Cleanups
1									
2									
3									
4									
5									
6									
7									
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GREAT LAKES ANALYTICAL

ATTACHMENT 2

EXTRACTION SUMMARY TABLE

	8015D-DR	8015T-TPH-D		8081/8082-Pesticides & PCBs		8151-Herbicides		8270-SVOC		8310-PNA	
Sample Matrix	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid
Sample Volum0e/Weight	1 L	1 L	30 g	1 L	30 g	1 L	30 g	1 L	30 g	1 L	30 g
Sample Preservative	HCl	none		none		none		none		none	
Surrogate Volume	50 µL	50 µL		1 Ml		1 mL		1 mL		1 mL	
pH	NA	NA		5-9		≤ 2	≤ 2	1) ≤ 2 2) ≥ 11	NA	NA	
Extraction Solvent	Hexane	$MeCl_2$		$MeCl_2$	1:1 Acetone - $MeCl_2$	Diethyl ether	1) $MeCl_2$ 2) KOH 3) Ether	$MeCl_2$		$MeCl_2$	
Extraction Solvent Volume, mL- (Replicates)	60 × 3	60 × 3	100 × 3	60 × 3	100 × 3	120, 60 × 2	1) 100 × 3 2) 15 × 3 3) 40, 20×2	1) 60 × 2 2) 60 × 2	100 × 3	60 × 3	100 × 3
Solvent Exchange or Final Solvent	none	Hexane		Hexane		Hexane		none		Acetonitrile	
Volume Solvent Exchange Added	NA	50 mL		50 mL		NA		NA		10 mL	
Nitrogen Blowdown	Yes	Yes		Yes		No		Yes		No	
Extract Final Volume	1 mL	1 mL		1 mL		10 mL		1 mL		10 mL	
Notes						Derivatize with diazomethane		Two extractions at each pH		Fill an additional autosampler vial	

Copy #: 8082-_____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY:

CAPILLARY COLUMN METHOD

GLA 8082 BG

Revision 1.1

Approved By:

Department Manager: _____ Date: 5-28-99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Manager: _____ Date: 5/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of polychlorinated biphenyls (PCBs) and related compounds by capillary gas chromatography (GC). This SOP is an interpretation of EPA method 8082. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples. Use method 8081 for samples for organochlorine pesticide analysis. If the matrix of these samples were environmentally degraded (*i.e.* "weathered"), pattern recognition of these analytes may require more detailed study.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Samples for PCB analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, see GLA SOP 3500 BG, sections 11.1 and 11.3).

Extracts are analyzed by capillary gas chromatography with electron capture detection (ECD). The GC is standardized to determine the recovery and limits of detection for the analytes of interest. Sample concentrations are determined by comparison to standard responses. Quantitative analysis is achieved through measurements of peak heights or integrations of peak areas.

This method is used to determine the concentrations of PCBs as Aroclors (mixtures). PCBs that can be detected by this method include Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260. The Aroclors are composed of various mixtures of 2-chlorobiphenyl, 2,3-dichlorophenyl, and the various isomers (congeners) of tri-, tetra-, penta-, hexa-, hepta-, and nona-chlorobiphenyls.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents, chemicals, and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 COEXTRACTED INTERFERENCES

Materials causing interferences may be coextracted from a sample. The extent of matrix interferences varies from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe or purging device should be rinsed out between samples with solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross contamination.

4.5 COELUTION

Coelution among the target analytes may cause interference. If this is suspected, standards of the individual analytes may be analyzed and retention times compared.

4.5 SULFUR

The presence of sulfur can result in broad peaks that interfere with the detection of early-eluting analytes. Sulfur contamination should be expected with sediment samples. Since the recovery of sulfur-containing pesticides (*e.g.* endosulfan) is reduced during sulfur cleanup, this compound is determined prior to cleanup.

4.6 INDUSTRIAL CHEMICALS

Other pesticides and industrial chemicals may cause interferences. For example, some coeluting organophosphorous pesticides can be removed using gel permeation chromatography (GPC) cleanup.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.
- Date and initals of analyst performing work.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each analysis. It has the method identification number on the outside cover. The contents of each book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and the internal standard control limits and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The name and concentration of the surrogate standard.

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used.
- Matrix type and method.
- Results complete with units.
- Comments.
- Analyst.

Each page is initialed and dated. Laboratory notebooks must be neat and legible. Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

5.4 STANDARD PREPARATION LOG

A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 6 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:

- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code(s) for the final solution(s). The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

6.0 QUALITY CONTROL

6.1 METHOD BLANKS

Method Blanks are prepared and analyzed to check for any laboratory contamination. For each matrix-specific extraction batch, a method blank is prepared. The method blank is taken through the identical extraction steps as the samples. Deionized water and clean sand are used as the blank matrix for water and soil, respectively. No target analytes should be detected above the requested reporting limit. If target analytes are detected in the method blank, and the same target analytes are not found in the samples, no corrective action is taken. If target analytes are detected in the method blank, and the same target analytes are found in the samples, all associated samples and QC are either reextracted, or the results are qualified.

6.2 INSTRUMENT BLANK

The instrument blank verifies that the analytical system is free from contamination - no contamination should be present in the blank above the reporting limit. The instrument blank must be quantitated before samples to verify that the system is "clean". If contamination is found, corrective action must be initiated. For example, samples run in that analysis sequence which contain the same contaminant are reanalyzed with a clean blank to confirm results, or the results flagged to indicate possible contamination.

6.3 CHECK STANDARD

Check standards validate the initial calibration curve and are used to gauge the daily operating condition of the instrument. The check standards contain the analytes at concentrations within the calibration range (mid-range). Periodically, a high or low standard may be used for this. The peaks are quantitated using the average RF for each compound calculated in the calibration study. Aroclor mixure 1016/1260 is used for initial verification of calibration (CCV).

The recovery of each peak in the check standard must be between 85 and 115 (100 ± 15) %. If the average recovery of the entire compound list is 100 ± 15%, then the method is considered "in calibration" for all compounds.

$$Recovery\ (\%) = \frac{calculated\ concentration}{concentration\ analyzed} \times 100$$

A check standard is analyzed once at a minimum of every 20 samples or every 12 hours. Each analytical run must end with the analysis of a check standard. The check standard is used to check chromatography for peak shape or co-elution problems. The check standard must be quantitated before the samples in the sequence to verify that the samples are being quantitated against a valid calibration. All sequences must be bracketed with passing check standards. Recoveries of all check standard analytes are documented in tables for tabulation of yearly statistical recovery limits.

6.4 SURROGATE STANDARD

Decachlorobiphenyl is employed as a surrogate standard to monitor the efficiency of the procedure. 0.5 µg of surrogate standard is added to all QC and test samples before extraction. The surrogate standard recoveries are tracked from all samples over a year to determine control limits. These limits are defined as the average recovery plus/minus 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are extracted and analyzed regularly to check the effect of the sample matrix on the performance of the method. The MS/MSD is a measure of the accuracy and precision of the method. Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

6.5.1 An MS/MSD is extracted and analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes samples are spiked with Aroclor 1016/1260 mixture at a final concentration of 33 µg/Kg and 1.0 µg/L, respectively.

6.5.2 Spike recoveries and percent differences of the duplicates for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries and percent differences must fall within the average spike recovery and percent difference over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 10 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.6 LABORATORY CONTROL SPIKES (LCS)

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

6.6.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) are spiked with Aroclor 1016/1260 mixture at a final concentration of 33 µg/Kg and 1.0 µg/L, respectively.

6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 LCSs. These limits should be posted by the analyst for reference.

For those extraction batches that do not have sufficient sample volume to extract the matrix spike in duplicate, the LCS is extracted in duplicate.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails.
- Contamination was present in the blank and in the sample.
- Recovery for QC sample outside of limits.

6.8 CONFIRMATION

All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column to verify the presence of the PCB(s). If sensitivity permits, GC/MS method 8270 may be used for confirmation (Full-scan GC/MS will normally require a minimum concentration of 10 ng/µL in the final extract for each single-component compound. GC/MS may not be used for confirmation when concentrations are less than 1 ng/µL in the extracts.) All QC requirements, including calibrations and retention time windows, must be fulfilled for the confirmation analyses. If the confirmation result differs from the original result by more than 40% and there is no evidence of chromatograqphic anomalies or interferences, then the higher value is reported, and the client is notified of the possible problem.

6.9 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8082 are queued under "EXTR" and "PCBS". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION

A calibration study determines the calibration factors (CFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram.

An Aroclor 1016/1260 mixture is used to demonstrate linearity of detection. A minimum of 5 concentration levels are used (a minimum of 5 representative peaks in each chromatogram are used for Aroclor identification and quantitation). The concentrations of the calibration standards are 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 µg/ml. A mid-range concentration standard is used for single-point calibration for PCBs other than 1016 and 1260.

Calibration factors (CF) are calculated by tabulating responses of each peak against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression (not forced through the origin, nor including the origin as a data point) is used to establish the equation of the calibration curve for that particular peak: *peak area = slope × concentration + constant.* Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. Add surrogate standard (0.05-1.0 µg/mL of TMX+DCB) to each level.
- For each peak, calculate:
* $CF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
* *Average and standard deviation for CFs*
* $\%RSD = \frac{\text{standard deviation of CFs}}{\text{average RF}} \times 100$

- If the %RSD is less than 20%, the average CF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 85 and 115%.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the concentrations determined for 7 spiked samples multiplied by the "t value" appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 samples is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if 0.20 µg/L of standard is injected, the calculated MDL must be between 0.02 and 0.20 µg/L. A MDL study is performed annually.

Procedure summary:

- Analyze 7 replicates of a spiked sample with low level standard (at or below lowest calibration level standard).
- Calculate the standard deviation for the results for the 7 replicates.
- Each MDL = standard deviation × 3.143.
- The calculated MDLs must be between 10 and 100% of the MDL standard.

(MDLs for Aroclors should vary in the range of 0.05 to 0.9 µg/L in water, and 57 to 70 µg/kg in soils.)

Note: MDL studies for multi-component compounds, such as the aroclors, are defined as the lowest concentration for which pattern recognition is possible. However, a traditional MDL study as described above is performed for the Aroclor 1016/1260 mixture.

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed when a new column is installed, or annually.

Procedure summary:
- Analyze the check standard three times over a 3 day period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time ± 3 × standard deviation.
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy.

Procedure summary:
- Analyze 4 replicate standards or spiked extracts.
- Recoveries of each compound must be between 70 and 130%.
- The %RSDs must be less than 20%.

9.0 EQUIPMENT

9.1 Gas chromatograph, consisting of:
- Column oven, electron capture detector (ECD) - Hewlett Packard 5890 or equivalent.
- Sample injector/controller - Hewlett Packard 7672 or equivalent.
- Analytical column - 30 m × 0.53 mm, DB-608 (J&W Scientific, no. 125-6837, or equivalent).
- Data collection and analysis system.

9.2 Glass syringes, various sizes.

9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Examples of standards include:

10.1.1 Surrogate standard - Restek Surrogate (no. 32000): deca-chlorobiphenyl (200 µg/mL); dilute 250 µL to 100 mL with acetone, for waste dilution samples, dilute 750 µL to 25 mL with acetone.

10.1.2 Spike standard - Mixture of Aroclors 1016 and 1260 at 1.0 µg/mL each.

10.1.3 Check standards (1000 µg/mL, in hexane, from Restek) -
- A. Aroclor 1221 (no. 32007)
- B. Aroclor 1232 (no. 32008)
- C. Aroclor 1242 (no. 32009)
- D. Aroclor 1248 (no. 32010)
- E. Aroclor 1254 (no. 32011)
- F. Aroclor 1260 (no. 32012)
- G. Working check standard - dilute 50 µL of 1000 µg/mL standard(s) to 50 mL with hexane.

10.1.4 Calibration standards (1000 µg/mL, in hexane, from Supelco) -

A. Aroclor 1016 (no. 90123R)
B. Aroclor 1221 (no. 90124R)
C. Aroclor 1232 (no. 90125R)
D. Aroclor 1242 (no. 90126R)
E. Aroclor 1248 (no. 90127R)
F. Aroclor 1254 (no. 90128R)
G. Aroclor 1260 (no. 90129R)

10.2 STANDARD DILUTIONS

Stock and working standards should be kept in a refrigerator between 0 and 10°C when not in use to preserve their integrity.

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.
C_2 = desired or calculated concentration of the working standard.
V_1 = volume of the stock standard diluted.
V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Place vial in refrigerator. The stock standard expires 3 months after opening, or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Standard Log.

10.4 WORKING STANDARD

Standards are prepared in hexane.

- Determine volumes of stock and working standard required.
- Fill volumetric flask about ¾ full with hexane.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date prepared.
  - Purpose (method).
  - Initials.
  - Expiration date.
  - GLA code.

The working standard expires 6 months after opening, or when the standard fails QC criteria, whichever is first. Preparation is documented in the Standard Log.

NOTE: A 5µL aliquot of a 10 ng/µL working standard is equivalent to 50 ng:
10 ng/µL × 5 µL = 50 ng

10.5 REAGENTS

10.5.1 Hexane - pesticide grade or equivalent.
10.5.2 Helium - ultra-high purity grade.
10.5.3 Nitrogen - ultra-high purity grade.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions.

11.1 ANALYTICAL SEQUENCE

Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with verification of instrument calibration, followed by sample extracts interspersed with QC samples, and ends with a check standard. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

11.2 RETENTION TIME WINDOWS

11.2.1 Retention time windows are adjusted daily using the results for each analyte in the check standard.

11.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (*e.g.* a dissimilar column) to verify the presence of the analyte(s).

11.3 GAS CHROMATOGRAPHIC OPERATING CONDITIONS

Temperature parameters

Injector:	250°C
Detector:	320°C
Oven program:	140°C for 2 min
	140 to 240°C at 10°C/min (10 min)
	240°C for 8 min
	240 to 260°C at 2.5°C/min (8 min)
	260°C for 1 min
	260 to 280°C at 15°C/min (1.3 min)
	280°C for 10 min

Gas flow

Column	~5 mL/min
Make-up	~50 mL/min

Injection

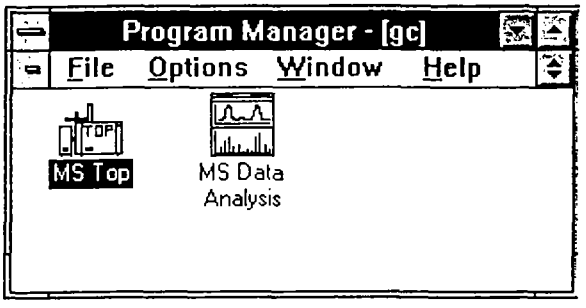
Volume	2 µL, splitless

See Figures 1 and 2 for example chromatograms.

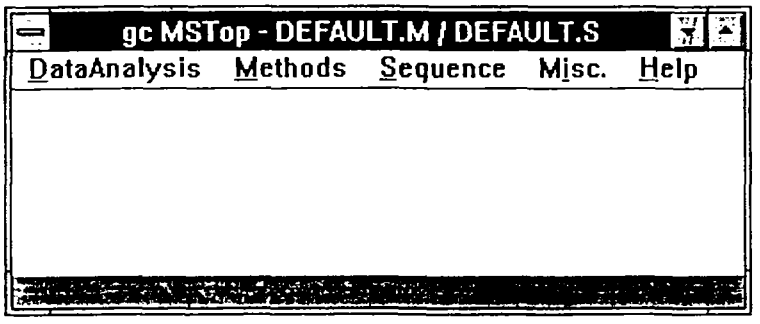
NOTE: Chromatographic conditions may be adjusted to give adequate separation of the characteristic peaks in each Aroclor. Once established, the same operating conditions are used for analysis of samples and standards.

11.4 SETTING UP A SEQUENCE IN ENVIROQUANT

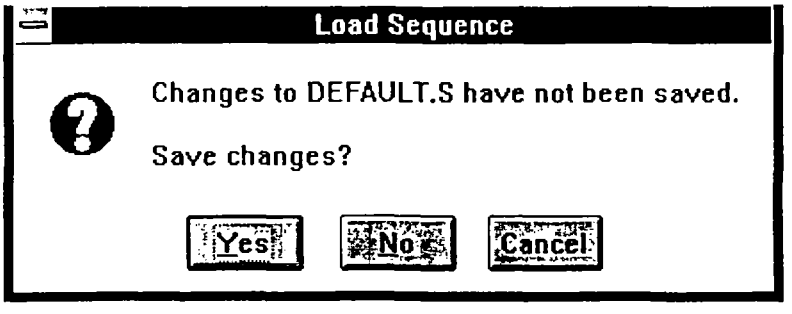
In Program Manager there is a group called GC-Enviroquant or GC/MS-#. Using the mouse, double click to open it and there will be an icon that looks like a GC.



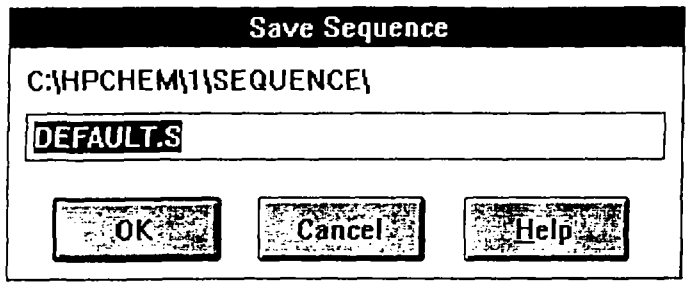
Double click on the GC icon to open it. (Note: Actual screen displays "GC Top" and "GC Data Analysis" icons.)



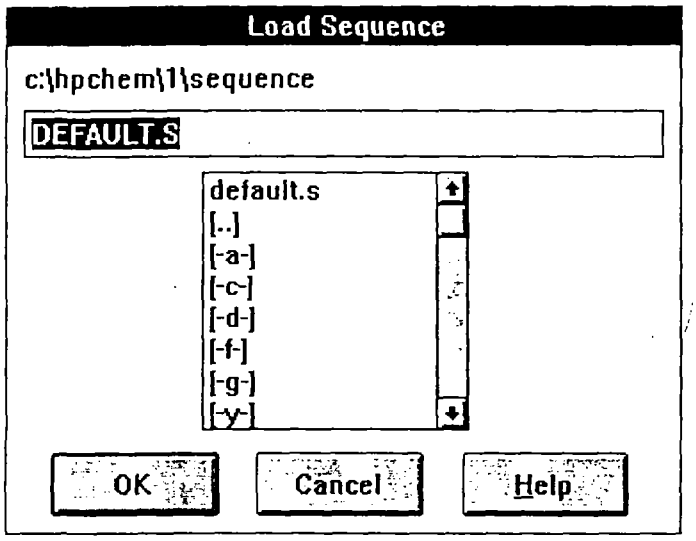
Click on the "Sequence" menu item and drag pointer to "Edit Sample Log Table".
Enter the sample information for each sample including Data File name, Method, and Sample Name.
The sample name is the LIMS information, which will look like:
GLA sample number|PCBS|8082|OK
Leave the miscellaneous field empty.
When this is done click on OK.
Go back to the "Sequence" menu and drag to "Load and Run Sequence".



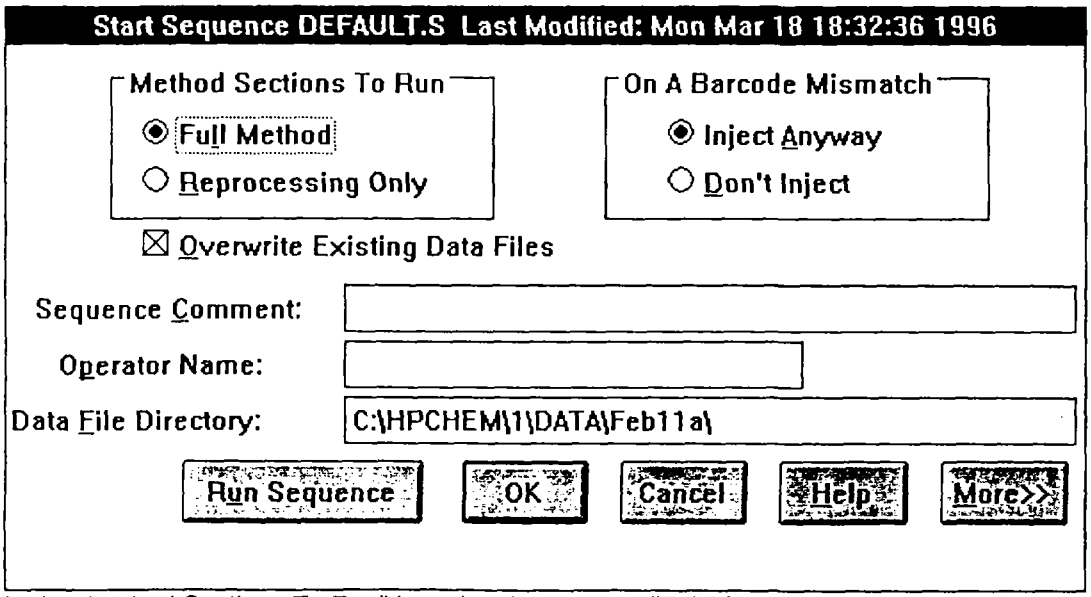
Click on "Yes".



Click on "OK".



Click on "OK".



In the "Method Sections To Run" box, the circle next to "Full Method" should be filled in.
In the "On A Barcode Mismatch" box, the circle next to "Inject Anyway" should be filled in.
The box next to "Overwrite Existing Data Files" should be checked.
In the "Operator Name" box, the analyst's initials that are used in LIMS are added.

In the "Data File Directory" field, after \DATA\, enter today's date or if the sequence was interrupted enter today's date with a letter appendage.
Click on Run Sequence.

11.5 QUANTITATION

11.5.1 When analyzing for Aroclors, a minimum of 3 peaks must be chosen for each Aroclor for pattern recognition. At least one of three peaks must be unique to the Aroclor of interest. At least 5 peaks are used for identity of Aroclor 1016/1260 mix. Every attempt should be made to avoid manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of standards constitutes fraud and is strictly forbidden.

11.5.2 If the responses exceed the concentration of the upper calibration standard, dilute the extract and reanalyze. If peak detection is prevented by the presence of interferences, further cleanup is required.

11.5.3 For reporting compounds that have been confirmed, the concentration of each analyte in the sample is determined by calculating the amount of standard injected, from the peak response, using the average calibration factor (CF) or linear regression calibration curve (section 8.1). These calculations may be done directly by the data collection and analysis software.

For aqueous samples:

Concentrations determined manually -

$$\text{Concentration } (\mu g/L) = \frac{A_x \times V_t \times D \times 1000}{CF \times V_s} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

A_x = peak area response for the analyte in the sample.
CF = average calibration factor.
V_t = volume of total extract (1 mL).
V_s = volume of sample extracted (1000 mL).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.
C = linear regression constant.
S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu g/L) = \frac{R_x \times V_t \times D \times 1000}{V_s}$$

Where:

R_x = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
V_t = volume of total extract (1 mL).
V_s = volume of sample extracted (1000 mL).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.

For soil/solid samples:

Concentrations determined manually -

$$\text{Concentration } (\mu g/kg) = \frac{A_x \times V_t \times D \times X \times 1000}{CF \times W} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times X \times 1000}{S \times V_s}$$

Where:

A_x = peak area response for the analyte in the sample.
CF = average calibration factor.
V_t = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1).
X= Percent solids (in decimal form; ex., 90%=0.90)
1000 = factor converting kilograms to grams.
C = linear regression constant.
S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu g/kg) = \frac{R_x \times V_t \times D \times 1000}{W}$$

Where:

R_x = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
V_t = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting kilograms to grams.

11.5.4 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

11.5.5 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%RPD = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.6 PARSING DATA TO LIMS

All PCB analyses are manually entered into LIMS, based on pattern recognition and quantitation.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

12.4 INJECTION PORT

When maintenance of the injection port is indicated, for example, by a loss of resolution and/or peak response. The port should be cleaned with hexane, and all replaceable parts exchanged. The column may also be checked for slugs of grease, etc., and these portions of the column removed.

12.5 COLUMN INSTALLATION

Column re-installation is necessary whenever maintenance is performed to the injection or detection ports. A new column is required when the baseline is elevated or the chromatography is poor (*e.g.* poor peak shape and/or low response).

For column installation, first slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to ensure that there are no jagged edges. The proper lengths of the column (to the base of the ferrule nuts) to be inserted into the injection and detection ports are 2.7 mm and 72 mm, respectively. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. Tighten the nuts.

New columns must be conditioned before method validation: Leave the column disconnected from the detection port. Ramp the oven temperature up to just below its maximum, at 1°C/min, and hold for 4 hours.

12.6 COLUMN RINSING

The GC column may be rinsed with several column volumes of appropriate solvents (both polar and non-polar). Depending on the nature of the sample residues expected, the first rinse could be water, followed by methanol and acetone. Methylene chloride is a good final rinse, and in some cases, may be the only solvent required. The column should then be filled with methylene chloride and stored overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen gas.

13.0 REFERENCES

13.1 EPA Method 8000B: Gas Chromatography.
13.2 EPA Method 8082: Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography.
13.3 Great Lakes Analytical Quality Assurance Program.
13.4 Great Lakes Analytical Chemical Hygiene Plan.
13.5 Great Lakes Analytical SOP for Login Department.
13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

Figure 1.

Example Chromatogram for Aroclor 1016/1260 Mixture.

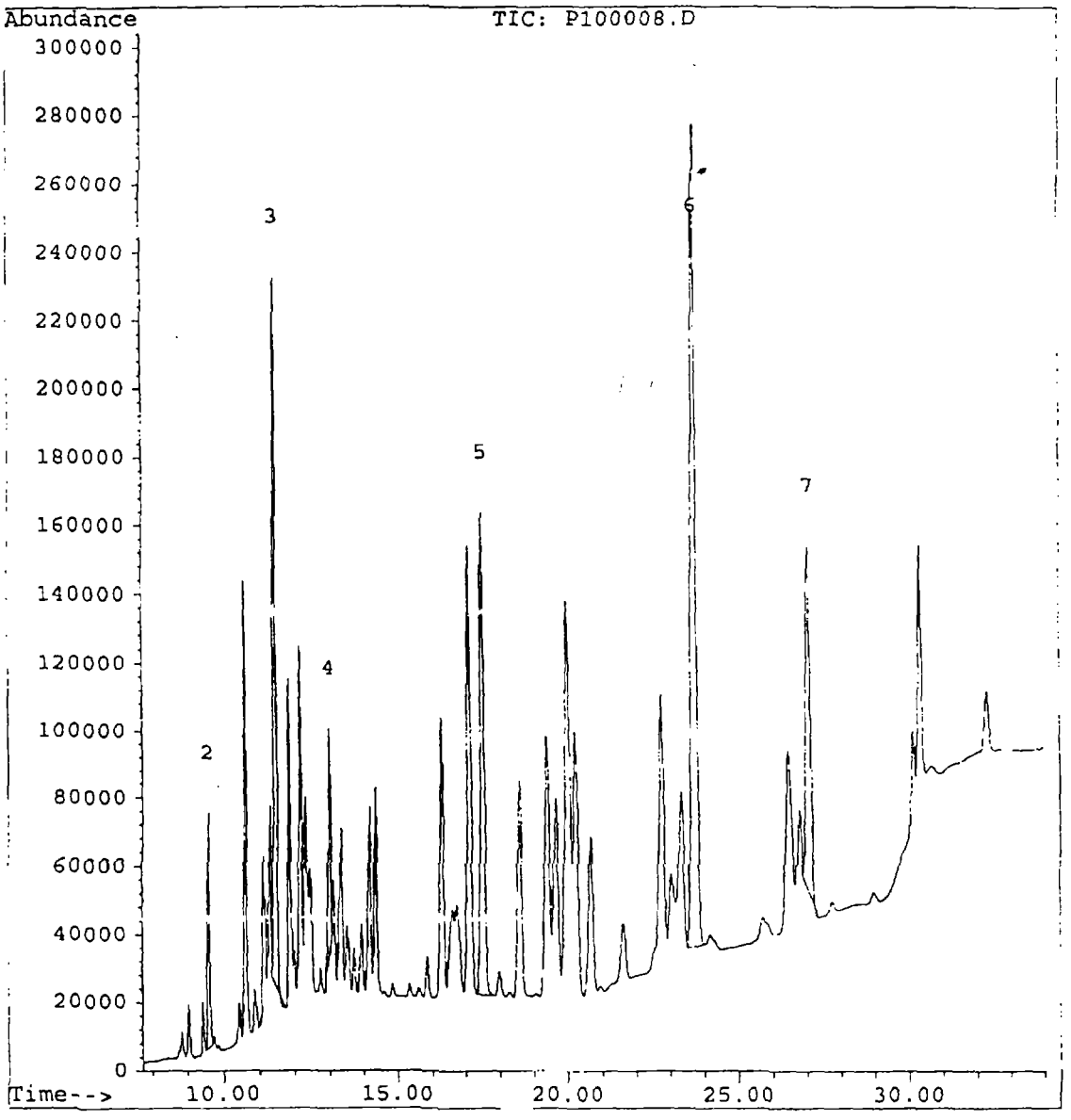
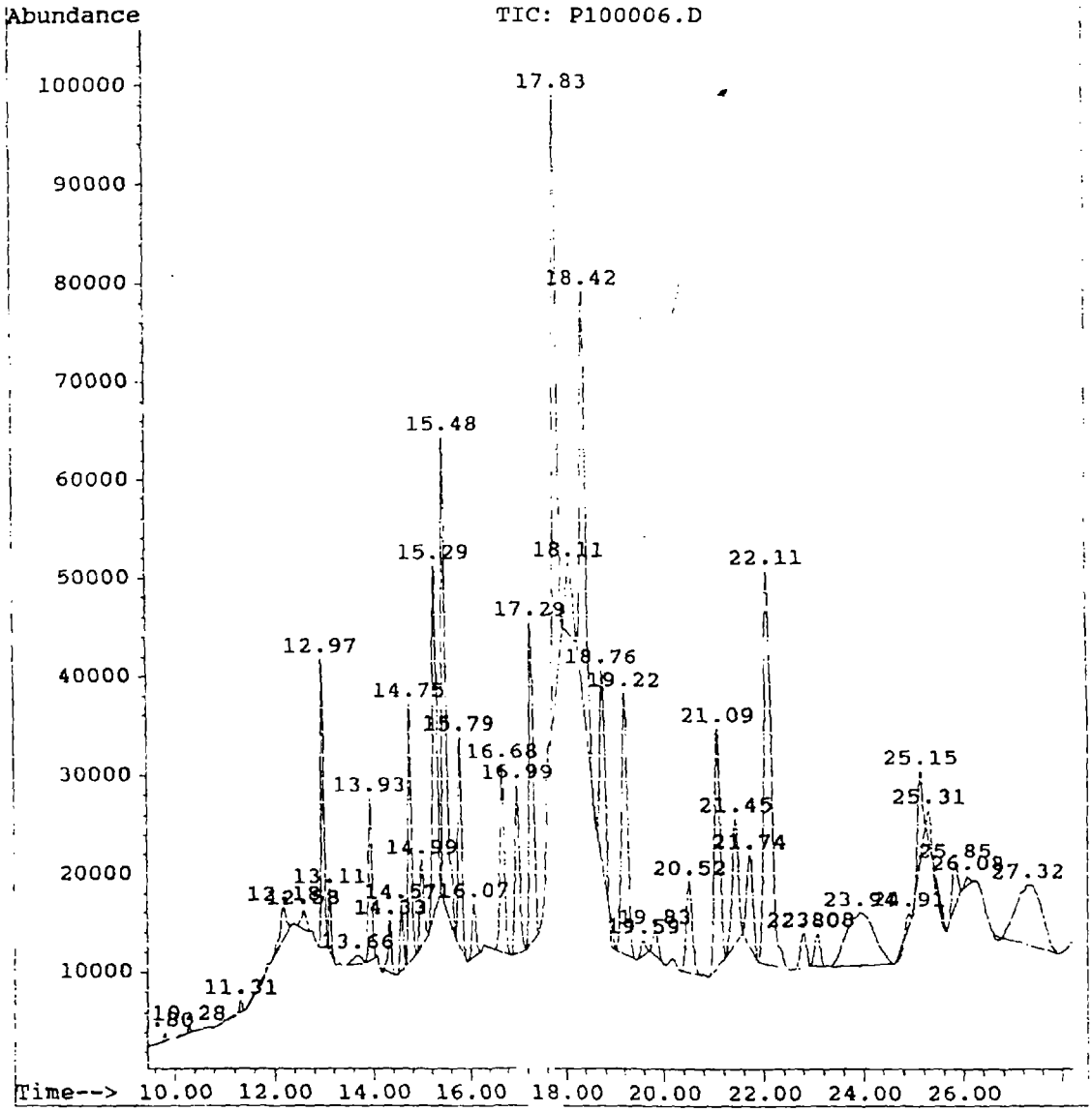


Figure 2.

Example Chromatogram for Aroclor 1254 Mixture.



DATA REVIEW

		YES	NO	CA	FLAG
1	Check standard recoveries within ± 15 % ?				
(8081) 1b	Prime and blank run?				
(8081) 1c	Endrine DDT breakdown < 15 % ?				
(8270) 1d	DFTPP tune evaluated and passing?				
(8270) 1e	SPCC average response factor > 0.050 ?				
(8270) 1f	CCC % deviation > 20 % ?				
(8270) 1g	Internal recoveries within 50-100 % ?				
2	Method blank recoveries < reporting limits?				
3	LCS within control limits?				
4	MS/MSD within control limits?				
5	All surrogate recoveries within control limits?				
6	All hits out of cal range diluted and re-analyzed?				
7	All sample holding times met?				
8	No transcription errors?				
9	No calculation errors?				

COMMENTS:

Analyst review signature: _____ Date: _____

Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and Reporting Limits (RL)

Method: PCBs by 8082

Analyte	Water (µg/L)			Soil (µg/Kg)		
	MDL	PQL	RL	MDL	PQL	RL
Aroclor 1016	0.0987	0.350	0.5	2.18	7.70	25
Aroclor 1260	0.0658	0.227	0.5	3.27	11.6	25
Aroclor 1221 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1232 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1242 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1248 (*)	0.10	NA	0.5	3.33	NA	25
Aroclor 1254 (*)	0.10	NA	0.5	3.33	NA	25

(*)--This compound is a multi-component analyte. The MDL for this analyte is based on the lowest concentration at which pattern recognition can be performed.

Copy #: 8260 -____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

BY PURGE-AND-TRAP AND

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GLA 8260 BG

Revision 2.1

Approved By:

Department Manager: _____ Date: 5/28/99

Quality Assurance Manager: _____ Date: 5/28/99

Laboratory Director: _____ Date: 5/28/99

1.0 APPLICABILITY

This procedure provides instructions for the analysis of samples for volatile organic compounds by a purge and trap extraction, followed by analysis with a gas chromatograph/mass spectrometer. This SOP is an interpretation of the SW-846 methods 8260B, 5030B, and 5035. It is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan, and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to water, soil, waste, and TCLP/SPLP matrices.

1.2 REGULATORY APPLICABILITY

40 CFR 121 (SW 846)

2.0 SUMMARY

This procedure describes the determination of volatile organic compounds by purge-and-trap, gas chromatography, and mass spectrometry. Helium is bubbled through a sample, purging out volatile components. These analytes are adsorbed onto a sorbent column (carbon trap). The trap is rapidly heated and backflushed with helium, desorbing the analytes onto a capillary column in a gas chromatograph. Once on the column, the analytes are separated by their interaction with the stationary phase of the column and the temperature program of the GC oven. The sample stream is reduced by a jet separator or a narrow bore restrictor column as it goes into the mass spectrometer. As analytes enter the detector, they are ionized by an ion source. Electrons fractionate the molecules, forming positive ions. Lenses focus the ion stream as it enters mass filtering quadrapoles. Varying AC and DC electronic signals on the quadrapoles permit ions with only certain mass to charge (m/z) ratios through the field. The filtered ion stream is then focused by another lens as it strikes the electron multiplier. The electron multiplier liberates neutralizing electrons that are proportional to ion abundance upon impact of the ion stream. The result is a total ion chromatogram as analytes are separated by the column with corresponding mass spectra in each peak. The peaks are identified by retention time and ion ratios. Each compound is assigned a primary characteristic ion. The area of this ion within its analytical peak is called an extracted ion current profile, or EICP of the characteristic ion. Quantitation is based upon generating response factors in a calibration study using EICP's for all compounds within the total ion chromatogram. Compounds which may be detected by this method are given in Appendix A.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves and safety glasses are worn when handling solvents, chemicals, and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.5 STANDARDS

The standards used for calibrations and quality control are known pollutants; therefore caution should be taken when handling them. Standard preparation should take place in a hood or well-ventilated area. Gloves will be worn when handling standards. Benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride are tentatively classified as known or suspected human or mammalian carcinogens, and should be handled accordingly.

4.0 INTERFERENCES

4.1 CONTAMINATION

Samples can become contaminated in the field or in transit. If trip and field blanks are analyzed with the sample group they can serve as a check for this type of contamination. A trip blank is a voa vial full of water that has accompanied the samples in transit. A field blank is a voa vial of reagent water that is poured through all the field equipment used in sampling. Contamination of samples can also occur during analysis from residue left by other samples in syringes, lines and glassware in the purge-and-trap, autosampler, column, or detector. A blank must be run through the analytical system every 12 hours to demonstrate that it is clean.

4.2 CARRYOVER

There are several ways residue, especially from a concentrated sample, can carryover into subsequent samples:

4.2.1 Trap carryover - All volatile components of a sample may not be sufficiently desorbed or baked off the trap, leaving residual hydrocarbons or specific analytes on the trap. These contaminants may come off the trap during the next run.

4.2.2 Glassware carryover - All volatile components may not be purged from the sample, leaving residual hydrocarbons or specific analytes in the glassware. These contaminants can be purged out with the next sample run in that position.

4.2.3 Line carryover - In a very concentrated sample, it is possible that the lines of the autosampler or purge-and-trap may become contaminated. This is evident when subsequent runs contain the same contaminant.

4.2.4 Column carryover - All of the hydrocarbons in a sample may not come off the column by the time the oven temperature program has finished. They elute as broad peaks in the next run.

If carryover is suspected for any reason, a blank should be run to verify a clean analytical system and any affected samples should be rerun. Individual autosampler positions should be baked out or have blanks run through them as necessary.

It is recommended that each purge-and-trap system have a "bake out" method that is performed before each analytical run. In this method, the line temperatures of the autosampler and the purge-and-trap are elevated and the autosampler positions are purged and baked without the addition of sample.

Syringe contamination and possible contamination from the extraction procedure are easily eliminated by rinsing syringes with water and spatulas with methanol between samples.

4.3 SAMPLE INTEGRITY

4.3.1 Samples submitted for volatiles analysis are kept at 4°C before analysis.

4.3.2 Water samples should be preserved with 1:1 hydrochloric acid in the field to pH<2 to kill any micro-organisms that may degrade the volatile aromatic compounds. Sample vials should be filled so that no headspace or air bubbles exist in the vial.

4.3.3 Soil samples are preserved based on the desired reporting limits. Low level soils are collected in containers that contain an aqueous solution of sodium bisulfate (1g of sodium bisulfate in 5ml water) as the preservative. High level soils are collected in containers which contain methanol as the preservative. Alternatively, soils may be collected in EnCore samplers, and sent to the lab for immediate transfering (within 48 hours of sampling) into vials with the appropriate preservative.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each instrument. It has the instrument identification number on the outside cover. The contents of this book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP's and the source methods.

- Copies of the calibration studies and internal standard control limits and the dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

5.3 RUN LOG

On the front cover of the Run Log notebook display:

- Instrument identification number.
- Run log number.
- Effective dates.

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample analyzed with units.
- Method number.
- Results complete with units.
- Status of internal and surrogate standard recoveries.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.).
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'd out.

5.4 SAMPLE SCHEDULE (LIMS)

Analysts keep track of sample throughput by using the LIMS (Laboratory Information Management System). The system is checked daily and all pertinent sample information is recorded, and a hard copy is generated. This information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time / turnaround time.

5.5 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all the standards prepared for the volatiles methods. Document in this book:

- Analyte, Purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Volume diluted.
- Expiration date of stock standard - six months after the standard has been opened or the date set by manufacturer, whichever is first. Gas stock standards are good for one month after opened, or until the date set by the manufacturer, whichever is sooner.
- Final concentration.
- Volume prepared.
- Date prepared.
- Expiration date of working standard - three months after the standard has been made or when standard fails Quality Control criteria, whichever is first. Gas working standards expire after two weeks.
- GLA code for the final solution. The GLA code is a number and letter sequence used to track standard preparation within the department. It consists of the month number and successive letter of the alphabet starting with "A" at the beginning of each month.
- Initials.

5.6 BALANCE LOG

A balance log is kept to check the accuracy of the scale used in soil sample extractions. Entries are made on any day the scale is utilized. Record:

- Date.
- Weight of the Class P check weight less the tared weight.
- Scale reading.
- Weight of second Class P check weight less the tared weight.
- Scale reading.
- Initial each entry.

Any problems and corrective action taken should also be recorded in this log.

6.0 QUALITY CONTROL

6.1 BFB TUNE CHECK

6.1.1 4-Bromofluorobenzene (BFB) must be analyzed at the start of every 12 hour sequence. 1µl (50ng) of the working tuning solution is directly injected onto the GCMS system.

6.1.2 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and is accomplished by using a single scan prior to the elution of BFB. Other techniques can be used as long as the apex is always included, and the other ions averaged are consecutive with the apex.

6.1.3 The key ions produced during the analysis of BFB and their respective ion abundance criteria are given below. This criteria must be met before any calibration standards, blanks, or samples can be analyzed.

Mass	m/z abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of 176

6.2 CALIBRATION VERIFICATION (CV)

The CV validates the initial calibration curve and is used to gauge the daily operating condition of the instrument. The CV (at 50 µg/L) is analyzed every 12 hours, after the 12 hour tune, but before actual samples are analyzed.

6.2.1 The minimum relative response factors (RRF's) of system performance check compounds (SPCC's) must meet method requirements:

SPCC's	Min. RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

$$RRF = \frac{EICP^{*} \text{ of analyte}}{\text{concentration of analyte}} \times \frac{\text{concentration of internal standard}}{EICP^{*} \text{ of internal standard}}$$

*of the characteristic ion

Note: When determining the RF, the internal standard used in the calculation is the one which elutes closest to the analyte.

6.2.2 Calibration check compounds (CCC's) must also meet specific criteria. The CCC's are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethyl benzene, vinyl chloride. For CCCs which are calculated by average response factor, the percent difference (%D) between the RF of the CCC compound and the corresponding average RF from the calibration curve must be $\leq$ 20%. For CCCs calculated by linear regression, the percent drift must be $\leq$ 20%. If the CCCs are not part of the target analyte list, then all target compounds must meet the 20% criteria.

$$\%\ Drift = \frac{\text{known concentration - calculated concentration}}{\text{known concentration}} \times 100$$

The CCV can be used to check chromatography for peak shape. The check standard must fulfill the above criteria before samples can be analyzed.

6.3 METHOD BLANK

The method blank verifies that the analytical system is free from contamination.

6.3.1 The method blank is run every 12 hours, after the CV, but before samples are analyzed.

6.3.2 No contamination should be present in the blank above the reporting limit. If contamination is found, samples analyzed after the blank which contain the same contaminates must be reanalyzed to confirm the detects.

6.3.3 The method blank may be the field blank sample submitted by a client for a particular project.

6.4 INTERNAL STANDARD

Internal standards are added to everything analyzed by this method. Recoveries are a factor in the concentration calculations of analytes. They also monitor the efficiency of the purge-and-trap extraction procedure.

6.4.1 The internal standards are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. The concentration of the internal standards is 50 ppb.

6.4.2 The retention times of the internal standards in the CVs must be within 30 seconds of retention times from the corresponding standard in the initial calibration.

6.4.3 The EICP areas of the characteristic ion of the internal standards in the CVs must be within 50% to 200% of those from the mid-point standard in the initial calibration.

6.4.4 When recoveries fall outside of the criteria, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, the data is reported from the original analysis and a corrective action form is filled out. If the recoveries of the internal standards fulfill criteria, the data from the re-analysis is reported.

6.5 SURROGATE STANDARDS

Surrogates are added to everything analyzed by this method. Surrogate standard recoveries are used to monitor the efficiency of the purge-and-trap extraction procedure.

6.5.1 The surrogate standards are dibromofluoromethane, 1,2-dichloroethene-d_4, toluene-d_8, and 4-bromofluorobenzene. The concentration of the surrogate standards is 50 µg/L.

6.5.2 The surrogate standard recoveries from 20 to 30 samples per matrix are tracked to determine the control limits. These limits are defined as the average recovery ± 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference. Limits are determined annually.

6.5.3 When surrogate standard recoveries fall outside these limits, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, results are reported from the original analysis and a corrective action form is filled out. If the recoveries fulfill criteria, data from the re-analysis is reported.

6.6 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are analyzed regularily to check the effect of the sample matrix on the performance of the method.

6.6.1 An MS/MSD is analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes contain all of the analytes on the compound list at a concentration of 50µg/L and 50 µg/Kg, water and soil respectively. TCLP spikes contain all of the analytes on the compound list at a concentration of 100 µg/L, except for 2-butanone, which is at 500 µg/L.

6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.7 LABORATORY CONTROL SPIKE (LCS)

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

6.7.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) is spiked at 50ppb with the same solution and at the same concentration as the MS/MSD.

6.7.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.8 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented. Examples of when corrective sheets are filled out are:

- Check standard recovery fails for a particular compound that was present in the sample.
- Contamination was present in the blank and in the sample.
- Internal standard recovery is outside of 50-200% limits.
- Surrogate recovery is outside of control limits.
- Matrix spike recoveries are outside of control limits.

6.9 CHECKLISTS

Checklists are designed to ensure that data being reported by the laboratory has met all of the daily quality control requirements. The analyst documents the status of all quality control requirements for an analytical batch by checking off and filling out Daily Batch Checklists prior to reporting results. If quality control criteria has failed, the analyst must document samples that were affected and whether or not corrective action was taken. (Please see attached checklists.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 HOLD TIME

7.2.1 Water samples preserved to a pH of less than 2 have a hold time of 14 days from the date sampled. Unpreserved water samples have a hold time of 7 days from the date sampled.

7.2.2 Soil samples received by the laboratory preserved with sodium bisulfate or methanol (see section 4.3) have a hold time of 14 days from the date sampled. Soil samples submitted to the lab in EnCore samplers, or in jars, must be preserved within 48 hours of sampling. Then, a holdtime of 14 days from the date of preservation is in effect.

7.2.3 Soil samples submitted for TCLP analysis must be zero headspace extracted within 14 days of sampling. An additional 14 day holdtime is in effect after the TCLP extraction has been performed.

7.2.4 If a sample is received or analyzed past the holdtime, the client is immediately informed of the problem, and the report is qualified.

7.3 SAMPLE SCHEDULE

Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8260 are queued under "VOMS". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

7.4 DISPOSAL

The analyst disposes of extracted samples one week after the date of analysis. Methanol and remaining fluid in the purge tubes is placed in the solvent drum. The login department maintains the other volatiles refrigerators. TCLP/SPLP extracts are disposed of one week after analysis. The extract is poured into the acid waste drum.

7.5 HAZARDOUS SAMPLES

If upon sample analysis analytes with concentrations above "Red Tag Limits" are found, the login department is notified by filling out a red tag sheet, and red tape is placed on the sample container. (See the GLA SOP for Hazardous Sample Management.)

RED TAG LIMITS

Compound	mg/kg	mg/L
Benzene	8	0.4
Carbon tetrachloride	8	0.4
Chlorobenzene	1600	80
Chloroform	96	4.8
1,2-Dichloroethane	8	0.4
1,1-Dichloroethene	11	0.56
Methyl ethyl ketone	3200	160
Tetrachloroethene	11	0.56
Trichloroethene	8	0.4
Vinyl chloride	3.2	0.16

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION STUDY

An initial calibration study determines the average response factors for the target and surrogate analytes that in turn are used to quantitate the concentration of these compounds in a sample. An internal standard calibration technique is employed in which the same concentration of internal standard is added to a series of freshly prepared calibration standards which encompass the linear range of the detector. The initial calibration must be developed before samples, blanks, and QC samples can be analyzed.

8.1.1 A minimum of five calibration levels are prepared and analyzed. For soil analysis, the calibration points are 5, 50, 100, 150, 200, and 250 µg/L. For water samples, the calibration points are 2, 10, 50, 100, 150, 200, and 250 µg/L. All target analytes, including surrogates, must be included in the each calibration level. Internal standards (at 50 ppb) are also added to each calibration level.

8.1.2 The RRFs are calculated (see 6.2.1) for each target analyte and surrogate in each calibration level. The average RRF is then calculated for all analytes, using all of the levels in the calibration study.

8.1.3 The average RRF's for the SPCCs must meet the minimum RRF requirements specified in section 6.2.1.

8.1.4 The percent relative standard deviation (%RSD) is calculated for all the analytes:

$$\%RSD = \frac{\text{standard deviation}}{\text{average RF}} \times 100$$

8.1.5 The %RSD for the CCCs (section 6.2.2) must be $\leq$ 30%.

8.1.6 If the %RSD is $\leq$ 15% for all included analytes, then the calibration is considered linear, and the average RRF is used for quantitating samples, blanks, and QC. However, if the %RSD exceeds 15%, a least squares linear regression curve must be created for each analyte above the 15%.

$y = mx + b$ where y = EICP area for the analyte
m = Slope of the curve
x = Concentration of the calibration standard
b = The y intercept of the curve

Note: The correlation coefficient generated by the regression must be $\geq$ 0.99 in order for it to be used for quantitation purposes.

8.1.7 If any of the above criteria is not met for the calibration, corrective action is performed, and another calibration study is analyzed.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the method detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported with 99% confidence. The MDL is equal to the standard deviation of the recoveries of seven aliquots multiplied by the analysts' t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The analysts' t value appropriate for 7 aliquots is 3.143. The calculated MDL

must be between 100% and 10% of the concentration of the MDL standard in order to be valid. An MDL study is done yearly per matrix.

- Run 7 replicate low level standards (at or below lowest calibration level standard).
- MDL = standard deviation x 3.143.
- The calculated MDL must be less than reporting limit.

8.3 ACCURACY AND PRECISION STUDY

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operation:

- Run 4 replicate standards at 50 µg/L.
- Recoveries of all compounds must be between 80-120%.
- The relative standard deviation must be less than 20%.

The study is performed by each analyst in charge of a new method, or when major maintenance is performed (changing a column, changing oven parameters).

9.0 EQUIPMENT

9.1 System 1 -

Purge-and-trap system:

- Tekmar LSC 2000 sample concentrator.
- Tekmar Archon autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carbopack B, 6 cm Carboxen 1001.

Operating parameters:

- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.
- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake: 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a Restek RTX-502.2 0.53 mm ID X 60 m column, Jet Separator interface and Hewlett Packard 5971 MSD. (GC/MS-1, Installed 7/91.)
Oven parameters:

- Mass spectrometer interface (Detector B) temperature: 250°C.
- Jet separator temperature (Detector A): 200°C.
- Injector temperature: 250°C.
- Temperature program: 36°C for 10 minutes increase 8°C/min. to 210°C, hold for 1 min.

Linear velocity of helium at 150°C: 59 cm/sec.
Column head pressure at 35°C: 6 psi.
Hewlett Packard Chemstation and Enviroquant Data Management System.

9.2 System 2 (for low level soils)-

Purge-and-trap system:

- Tekmar LSC 3000 sample concentrator.
- Tekmar 2016 Purge and Trap Autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carbopack B, 6 cm Carboxen 1001.

Operating parameters:

- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.

- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake : 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a J&W DB 624 0.53 mm ID X 75 m column, narrow-bore restrictor column interface, and Hewlett Packard 5972 MSD. (GC/MS-3, installed 10/94.)
Oven parameters:

- Mass spectrometer interface (Detector B) temperature: 250°C.
- Injector temperature: 250°C.
- Temperature program: 40°C for 10 minutes increase 8°C/min to 220°C hold for 3 min.

Linear velocity of helium at 110°C: 37 cm/sec.
Column head pressure at 35°C: 8 psi
Hewlett Packard Chemstation and Enviroquant Data Management System.

9.3 Mass Spectrometer Parameters

Scan range : 35 to 400 amu
Scan Rate : 2.08scans/second

Specific instrument parameters can be found in the instrument maintenance log.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards are ordered from EPA or A2LA Certified companies. These companies include Accustandard, Restek, Supelco, and Ultra Scientific.

10.2 STANDARD DILUTIONS

Standards are volatile so special care should be taken to preserve their integrity. Stock and working standards are kept in a freezer between -10 and -20°C when not in use.

A useful equation for standard preparation is:

$$C_1V_1 = C_2V_2$$

Where:
C_1 is the initial concentration of the stock standard.
C_2 is the desired concentration of the working standard.
V_2 is the volume of working standard to be prepared.
V_1 is the volume of stock standard to be diluted.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with Teflon-lined cap. Label this vial with:
Analyte description.
Manufacturer.
Lot number.
Concentration.
Date opened.
Expiration date.

Store in a freezer. The stock standard expires six months after it is opened or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Volatile Standard Log.

10.4 WORKING STANDARD

Standards are diluted in methanol:

- Fill a volumetric flask about three quarters of the way full with methanol.
- Add desired amount of stock standard.
- Fill volumetric flask to meniscus.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date made.
  - Purpose.
  - Initials.
  - Expiration date.
  - GLA code.

The working standard expires three months after it is opened or when the standard fails Quality Control Criteria, whichever is first. Preparation is documented in the Volatile Standard Log.

10.5 REAGENTS

10.5.1 Methanol - Purge-and-trap grade methanol is used for extractions and standard preparation.

10.5.2 Reagent water – Bottled drinking water is boiled for three minutes and then purge with nitrogen before use in analyses.

10.5.3 Gases - Ultra-high purity grade helium.

11.0 PROCEDURE

11.1 Before samples can be prepared for loading onto the instrument, all utensils must be cleaned. Syringes used for fortifying samples are rinsed several times with purge and trap grade methanol. 5ml syringes are rinsed several times with reagent grade methanol and twice with reagent water. Purge vessels are also rinsed several times with reagent grade methanol, and twice with reagent water.

11.2 Before anything can be loaded and analyzed, the purge and trap autosampler must be cleaned. This involves flushing the sample valves and sparger needles with several mls of a 1:1 water/methanol mix. A plastic 25ml syringe is twisted onto the sample valve, the valve is opened, and several mls of the mix is injected through the valve and collected at the end of the sparger needle with a 500 ml plastic beaker. The sparger needle is wiped clean with a kimwipe. This process is repeated for each autosampler port.

11.3 If highly concentrated samples (eg. exceed the calibration range) have been analyzed on the instrument (on column concentrations > 400 ppb), a bake-out procedure is required. This involves purging each port for 2 minutes and heating each sample line to 180 °C. Consult instrument maintenance procedures for complete details.

11.4 A typical analytical run would be as follows:

BFB Tune
Calibration Std #1
Calibration Std #2
Calibration Std #3
Calibration Std #4
Calibration Std #5
} Analyze calibration curve as needed
CV
Method Blank
QC Check Sample
Sample Analysis (# of samples dependent on 12 hour clock)
MS (per 20 samples or less by matrix)
MSD (per 20 samples or less by matrix)

11.5 All of the following procedures and the order of analysis must be documented in the Volatiles Run Logbook.

11.6 Before analyzing calibration standards, CVs, blanks, QC, and samples, a BFB tune is analyzed by injecting the appropriate amount of the working BFB tune solution (50 ng on-column). All the criteria in Section 6.1.3 must be met before proceeding with the typical run outlined above.

11.7 After an acceptable BFB tune has been analyzed, an initial calibration is prepared and analyzed. A minimum of five calibration standards are prepared in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler), and analyzed from low (5ppb) to high (400ppb) concentration. All the criteria in Section 8.1 must be met before samples can be analyzed.

11.8 Once an initial calibration is established, a CV is prepared (@50ppb) in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler) and analyzed. All the criteria in Section 6.2 must be met before samples can be analyzed.

11.9 Next, a method blank is prepared in 5 ml reagent water (5ml sodium bisulfate preservative solution for Archon autosampler) by fortifying the water with internal standard and surrogate only (@ 50ppb). The analytical results must fulfill Section 6.3 before samples can be analyzed.

11.10 Finally, an LCS is prepared (@50ppb) in 5 ml reagent water (5ml sodium bisulfate preservative solution with ~ 5.0g clean sand for Archon autosampler), or 5g of clean sand (med/high level soils), and analyzed. The recovery limits described in Section 6.7 should be fulfilled.

11.11 Once 11.6 through 11.10 have been completed, samples can be analyzed.

11.2 Water Sample Analysis

11.2.1 All samples are removed from the volatiles storage refrigerator and allowed to reach room temperature.

11.2.2 Water samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with the sample.

11.2.3 The plunger is placed into the barrel, and the volume is adjusted to 5ml, taking care of eliminating any air bubbles in the syringe.

11.2.4 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.

11.2.5 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each syringe.

11.2.6 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.

11.2.7 After a water sample has been loaded, the pH of the sample is taken by dipping a pH strip into the opened sample vial. The pH is recorded in the Volatiles Run Logbook.

11.3 TCLP/SPLP Sample Analysis

11.3.1 After the samples are leached by the zero headspace technique, samples are given to the Volatiles group for analysis.

11.3.2 Leached samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with reagent water.

11.3.3 The plunger is placed into the barrel, and the volume is adjusted to 4.75ml, taking care of eliminating any air bubbles in the syringe.

11.3.4 Then, 250µl of the leached sample is added to the syringe.

11.3.5 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.

11.3.6 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each syringe.

11.3.7 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.

11.4 Low Level Soil Analysis

This procedure is used for samples preserved with sodium bisulfate. Estimated concentrations for this procedure are projected to be < 200 µg/Kg.

11.4.1 The exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative and stir bar from the vial containing the preservative, stir bar, and soil.

11.4.2 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.

11.4.3 The sample vials, containing ~5.0g of soil, 5ml of the sodium bisulfate preservation solution, and a stir bar, are gently shaken to insure free flowing of the sample for stirring. Vials are then placed into the Archon autosampler.

11.4.4 The autosampler then automatically adds 10ml of reagent water, and 1µl of the internal standard/surrogate solution (final conc.=50ppb).

11.4.5 The contents of the vials are preheated to 40°C, and then stirred and purged for 11 minutes. The purge effluent is then transferred onto the sorbent trap of the concentrator, and in turn, desorbed into the instrument for analysis.

11.4.6 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is manually added through the vial septum using a gastight syringe.

11.4.7 If concentrations of target analytes exceed the calibration range, an alternative analytical procedure is required (high level soil analysis).

11.5 Medium/High Level Soil Analysis

This procedure is used for methanol preserved soil samples, or for unpreserved soils and waste samples that are expected to have concentrations of target compounds in excess of 200µg/Kg.

11.5.1 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.

11.5.2 For methanol preserved samples, the exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative from the vial containing the preservative and soil. The standard methanol to soil for preserved samples is 2:1; however, 1:1 ratio is also an acceptable ratio. Moreover, a definite ratio is needed in order to determine the dilution factor for the extraction. Proceed to 11.16.5.

11.5.3 For unpreserved soils, or waste samples, 10.0g (+/- 0.05g) of sample is weighed into a clean extraction vial. 5ml of methanol is added to the vial. This preparation is documented in the Extraction Logbook. Other sample and methanol amounts can be used; however, the ratio chosen must result in a total submerging of the sample by the methanol.

11.5.4 Before samples are extracted, the appropriate amount of surrogate is added to each vial, so that the resulting on-column concentration is 50µg/Kg. Since this addition could effect the ratio of methanol to soil, good documentation is needed. An addition of $\leq$100µl of the surrogate solution is negligible.

11.5.5 Shake the sample vials for two minutes, and allow to settle.

11.5.6 While the sample is settling, fill a 5ml syringe to 4.9ml with reagent water.

11.5.6 Once the sample has settled, remove a 100µl aliquot of the methanol extract, and add it to the 5ml syringe prepared in 11.16.7. Then, add the appropriate amount of internal standard (50µg/Kg).

11.5.7 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to the vials before extraction, keeping in mind the methanol/sample ratio.

11.4.4 The autosampler then automatically adds 10ml of reagent water, and 1µl of the internal standard/surrogate solution (final conc.=50ppb).

11.4.5 The contents of the vials are preheated to 40°C, and then stirred and purged for 11 minutes. The purge effluent is then transferred onto the sorbent trap of the concentrator, and in turn, desorbed into the instrument for analysis.

11.4.6 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is manually added through the vial septum using a gastight syringe.

11.4.7 If concentrations of target analytes exceed the calibration range, an alternative analytical procedure is required (high level soil analysis).

11.5 Medium/High Level Soil Analysis

This procedure is used for methanol preserved soil samples, or for unpreserved soils and waste samples that are expected to have concentrations of target compounds in excess of 200µg/Kg.

11.5.1 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.

11.5.2 For methanol preserved samples, the exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative from the vial containing the preservative and soil. The standard methanol to soil for preserved samples is 2:1; however, 1:1 ratio is also an acceptable ratio. Moreover, a definite ratio is needed in order to determine the dilution factor for the extraction. Proceed to 11.16.5.

11.5.3 For unpreserved soils, or waste samples, 10.0g (+/- 0.05g) of sample is weighed into a clean extraction vial. 5ml of methanol is added to the vial. This preparation is documented in the Extraction Logbook. Other sample and methanol amounts can be used; however, the ratio chosen must result in a total submerging of the sample by the methanol.

11.5.4 Before samples are extracted, the appropriate amount of surrogate is added to each vial, so that the resulting on-column concentration is 50µg/Kg. Since this addition could effect the ratio of methanol to soil, good documentation is needed. An addition of $\leq$100µl of the surrogate solution is negligible.

11.5.5 Shake the sample vials for two minutes, and allow to settle.

11.5.6 While the sample is settling, fill a 5ml syringe to 4.9ml with reagent water.

11.5.6 Once the sample has settled, remove a 100µl aliquot of the methanol extract, and add it to the 5ml syringe prepared in 11.16.7. Then, add the appropriate amount of internal standard (50µg/Kg).

11.5.7 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to the vials before extraction, keeping in mind the methanol/sample ratio.

11.5.8 All sample results must fall within the established calibration range. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Samples are diluted further by varying the amount of extract added to the purge water. The amount of extract added must be $\geq$ 10µl and $\leq$ 100µl. For larger dilutions, serial dilutions of the extract are performed using volumetric flasks.

11.6 General Analysis Notes

11.6.1 Each analytical batch must be completed within a 12 hour time frame. Any analysis performed outside the 12 hour clock must be reanalyzed. The twelve hour clock starts at the time of the BFB tune.

11.6.2 All compounds must fall within the established calibration range, unless the client allows sample results to exceed the calibration range. Reported results which exceed the calibration range are flagged as estimated.

11.6.3 If exceedance of the calibration range is allowed, reanalysis is still required if the exceeding result is below the requested reporting limit.

11.6.4 If a sample is analyzed immediately following a highly concentrated sample, reanalysis of the sample should be considered.

11.6.5 If a highly concentrated sample (>400 ppb for any target compound) is analyzed on a port, instrument blanks must be analyzed in that port until analytical results show no detection above the reporting limit. An instrument blank is prepared the same as a method blank.

11.7 Qualitative Analysis

11.7.1 Qualitative identification of compounds is based on relative retention time (RRT) and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Appendix A lists the characteristic ions for all the target compounds.

11.7.2 The RRT of the suspected constituent in the sample must be within $\pm$ 0.06 RRT units of the RRT of the standard compound.

11.7.3 The intensities of the characteristic ions of a compound should maximize in the same scan, or within one scan of each other. This is determined automatically with the data systems target compound search routine.

11.7.4 The relative intensities of the characteristic ions should agree within 30% of the relative intensities of these ions in the reference spectrum (ex. For an ion abundance of 50% in the reference spectrum, the corresponding abundance in the sample spectrum can range between 20% and 80%).

11.7.5 For those isomer compounds that produce very similar mass spectra, the retention time should be used to identify the individual isomers.

11.7.6 If a compound cannot be verified by the above criteria, but in the technical judgement of the analyst, the identification is correct, then the compound shall be reported.

11.8 Quantitative Analysis

11.8.1 After a compound has been qualitatively identified following Section 11.18, the concentration of a target compound can be calculated based on the EICP area of the compound. Integration of EICP of the characteristic ion is performed automatically by the data system.

11.8.2 Manual integrations done specifically to meet method or contract quality control requirements are not permitted. There are situations when manual integration may be necessary, such as complex samples where partial coelution of peaks occur, or when the baseline has not been assigned adequately by the data system. In the instances, the trained analyst shall use their best technical judgement in the integration of the chromatogram.

11.8.3 The internal standard technique is used for quantitation (see Section 8.1). If the RSD from the calibration for a compound is ≤15 %, then the AvgRRF maybe used in the calculation of the concentration. If the RSD from the calibration for a compound is >15%, then the linear regression is used to calculate the concentration.

12.0 CALCULATIONS

12.1 Water Samples (using AvgRRF)

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\,(I_s)\,(DF)}{(A_{is})\,(\text{AvgRRF})\,(V_o)}$$

where:
A_x = Area of the characteristic ion of the compound
A_{is} = Area of the characteristic ion of the internal standard
I_s = IS amount in nanograms (ng)
AvgRRF =Average relative response factor from the calibration
V_o = Final volume of water purged in ml's (5ml)
DF =Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ration of the number of milliliters (mL) of water purged (i.e. Vo above) to the number of mL of the original water sample used for purging. For example, for TCLP samples, 0.25ml of sample is diluted to 5.0 mL with reagent water and purged --- DF=5.0mL/0.25mL = 20. If no dilution is performed, Df = 1.0.

12.2 Low Level Soils (Using AvgRRF)

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\,(I_s)}{(A_{is})\,(\text{AvgRRF})\,(V_o)}$$

where:
A_x = Area of the characteristic ion of the compound
A_{is} = Area of the characteristic ion of the internal standard
I_s = IS amount in nanograms (ng)
AvgRRF =Average relative response factor from the calibration
V_o = Final weight of soil purged in grams

12.3 Soil/Sediment/Waste Samples (using AvgRRF)

$$\text{Concentration } (\mu g/Kg) = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})\,(\text{AvgRRF})\,(V_i)\,(W_s)\,(D)}$$

where:
A_x , A_{is} , I_s and AvgRRF are the same as for the water calculation above
V_t = For Med/High level samples: Volume of total extract (µl)
V_i = For Med/High level samples: Volume of extract added for purging (µl)
W_s= Weight of sample extracted or purged (g)
D= % dry weight, where D= (100- %moisture)/100

12.4 Sample Quantitation by Linear Regresion: Samples which require quantitation from a linear regression calibration curve will follow the following general equation:

$$C = (m(A) + b) \times DF$$

where:
C= Concentration of the compound
m = Slope of the calibration curve
A = Ratio of the sample EICP area to the internal standard EICP area
b = Intercept of the calibration curve (based on order of regression used)
DF = Dilution factor (based on 5ml, 25ml, or 5g of sample purged)

12.5 Surrogate Percent Recovery

$$\% \text{ Recovery} = \frac{\text{concentration found}}{\text{concentration spiked}} \times 100$$

12.6 Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

where:
SSR = spiked sample result
SR = sample result
SA = spike added

12.7 Relative Percent Difference (RPD)

$$RPD = \frac{|(MSR - MSDR)|}{(1/2)(MSR+MSDR)} \times 100\%$$

where:
MSR = matrix spike recovery
MSDR = matrix spike duplicate recover

13.0 REPORTING NOTES

13.1 Data is reported in µg/kg or µg/L. This is equal to parts per billion, or ppb.

$$\frac{\mu g}{kg} = \frac{\mu g}{kg} \times \frac{1000\ ng/\mu g}{1000\ g/kg} = \frac{ng}{g}$$

$$\frac{\mu g}{L} = \frac{\mu g}{L} \times \frac{1000\ ng/\mu g}{1000\ mL/L} = \frac{ng}{mL}$$

13.2 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

13.3 If a sample is analyzed with dilution, a dilution factor needs to be applied to the reporting limit. Reporting limits are based on full strength sample aliquots of 5.0g for soils, 5.0ml for waters, and 250µl for TCLP extracts.

$$\textit{Dilution factor (DF)} = \frac{\textit{full strength}}{\textit{amount analyzed}}$$

$$\textit{Raised reporting limit} = \textit{reporting limit} \times DF$$

14.0 LIBRARY SEARCH

14.1 Tenatively Identified Compounds (TICs): To identify compounds which are not part of the targeted and calibrated list, a library search is performed on the mass spectra to determine tenative identification.

14.2 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

14.3 The relative intensities of the major ions should agree within ±20%(ex. For an ion abundance of 50% in the standard spectrum, the corresponding abundance in the sample spectrum can range between 30% and 70%).

14.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

14.5 Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or coelution of another compound.

14.6 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system.

14.7 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. Unknown hydrocarbon).

14.8 The 10 largest non-target peaks on the chromatogram are quantitated against the closest eluting internal standard. The RF for each unknown compound is assumed to be one.

15.0 INSTRUMENT MAINTENANCE LOG

15.1 It is very important to maintain an accurate and detailed instrument maintenance log. Document all problems and attempts at correcting them as well as results. This information is invaluable when the problem recurs and a clear solution.is laid out. Documentation of routine maintenance such as changing tanks and cleaning the detector can also provide insight into a subsequent problem.

16.0 TROUBLESHOOTING

16.1 When troubleshooting the system for a chromatography or sensitivity problems it is important to isolate the problem. Only change one thing at a time. A standard should be run after every change to see if any progress has been made. The instrument maintenance log should have all run parameters documented. Check these parameters to see if they have changed.

16.2 Direct Inject: A direct injection bypasses the purge-and-trap system. If the direct injection looks bad, the problem is with the gas chromatograph or the detector. If the direct inject looks good, then the problem probably is with the purge-and-trap system.

16.3 Checking flows: Attach flow meter to vent on the sample concentrator. Step to purge. Measure flow in ml/min. by using timer on GC.

16.4 Checking for leaks: Use the Gowmac leak detector at all unions in the injection port, in the detector, at the regulators on the GC or use methanol to see if it bubbles. To leak check the purge-and-trap, cap off the vent on the sample concentrator. Step the unit to purge. The sparge vessel should stop bubbling at about 7 minutes. If the instrument stops bubbling before 6 minutes there is a leak in gas lines before the sparge vessel. If the instrument

continues to bubble past 8 minutes there is a leak in the gas lines after the sparge vessel. The MSD can be set up to look for the mass of methanol. Enter the mass of methanol (31) into the scan parameters and squirt methanol around any unions. If there is leak the methanol mass peak will get larger as the methanol reaches the detector.

16.5 Column installation: Column re-installation is necessary whenever maintenance is done to the injection or detection ports. A new column is necessary when there is an elevated baseline or the chromatography is bad. To install a column, slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to insure that there are no jagged edges. Consult the instrument manual for the proper length of the column to be inserted into the injection or detection ports. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. If the column is new, it must be conditioned before it is ready for method validation. Leave the column disconnected from the detection port. Ramp the oven temperature up at 1°C/min. to just below its maximum and hold for 4 hours.

16.6 Other sources of problems

16.6.1 Trap - Indications of a bad trap are: benzene in the blank, decreased internal area, back-pressure in the autosampler, decreased carbon tetrachloride response.

16.6.2 Standards - Bad standards are easily detected by analyzing them on multiple I instruments.

16.6.3 Glassware - Indication of glassware or autosampler position problems include poor check standard or spike recoveries repeatedly in one position, poor surrogate and internal standard recoveries always in the same position.

16.6.4 Injection port - Due to the direct injections of BFB, it is often necessary to change the septa in the injection port so that there is not a leak.

16.6.5 Dirty detector - Indications of a dirty detector include: BFB will not pass specification; Low high mass abundance; High background; High EM voltage

17.0 REFERENCES

17.1 SW-846 Method 5030B: Purge-and-Trap for Aqueous Samples.
17.2 SW-846 Method 5035: Closed-System Purge-and-Trap and Extraction Volatile Organics in Soil and Waste Samples.
17.3 SW-846 Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry.
17.4 Great Lakes Analytical Quality Assurance Program Manual.
17.5 Great Lakes Analytical Chemical Hygiene Plan.
17.6 Great Lakes Analytical SOP for Login Department.
17.7 Great Lakes Analytical SOP for Hazardous Sample Management.

APPENDIX A.

DETECTABLE COMPOUNDS.

	Primary Characteristic Ion
Acetone[a,b]	58
Acrolein	56
Acrylonitrile	53
Benzene[a,b]	78
Bromobenzene	156
Bromochloromethane	128
Bromodichloromethane[a]	83
Bromoform[a]	173
Bromomethane[a]	94
2-Butanone (MEK)[a,b]	72
n-Butylbenzene	91
sec-Butylbenzene	105
tert-Butylbenzene	119
Carbon disulfide[a,b]	76
Carbon tetrachloride[a,b]	117
Chlorobenzene[a,b]	112
Chlorodibromomethane[a]	129
Chloroethane[a]	64
2-Chloroethylvinyl ether[a]	63
Chloroform[a]	83
Chloromethane[a]	50
2-Chlorotoluene	91
4-Chlorotoluene	91
1,2-Dibromo-3-chloropropane	75
1,2-Dibromoethane	107
Dibromomethane	93
1,2-Dichlorobenzene	146
1,3-Dichlorobenzene	146
1,4-Dichlorobenzene	146
Dichlorodifluoromethane	65
1,1-Dichloroethane[a]	63
1,2-Dichloroethane[a]	62
1,1-Dichloroethene[a]	96
cis-1,2-Dichloroethene[a]	96
trans-1,2-Dichloroethene[a]	96
1,2-Dichloropropane[a]	63
1,3-Dichloropropane	76
2,2-Dichloropropane	77
1,1-Dichloropropene	75
cis-1,3-Dichloropropene[a]	75
trans-1,3-Dichloropropene[a]	75
Diisopropyl ether	45
Ethyl benzene[a,b]	91
2-Hexanone[a]	43
Hexachlorobutadiene	225
Isopropyl benzene	105
p-Isopropyltoluene	119
4-Methyl-2-pentanone (MIBK)[a,b]	100
Methylene chloride[a,b]	84
Methyl tert-butyl ether	73
2-Nitropropane[b]	46
Naphthalene	128
n-Propylbenzene	91
Styrene[a]	104
1,1,1,2-Tetrachloroethane	131
1,1,2,2-Tetrachloroethane[a]	83
Tetrachloroethene[a,b]	164
Tetrahydrofuran	42
Toluene[a,b]	92
1,2,3-Trichlorobenzene	180
1,2,4-Trichlorobenzene	180
1,1,1-Trichloroethane[a,b]	97
1,1,2-Trichloroethane[a,b]	83
Trichloroethene[a,b]	95
Trichlorofluoromethane[a,b]	151
1,1,2-Trichloro-1,2,2-trifluoroethane[b]	101
1,2,3-Trichloropropane	75
1,2,4-Trimethylbenzene	105
1,3,5-Trimethylbenzene	105
Vinyl acetate[a]	43
Vinyl chloride[a]	62
m,p,o-Xylenes[a,b]	106
Methyl iodide	142
Internal standards:	
Pentafluorobenzene	168
1,4-Difluorobenzene	114
Chlorobenzene-d_5	117
1,4-Dichlorobenzene-d_4	152
Surrogate standards:	
Dibromofluoromethane	113
1,2-Dichloroethane-d_4	65
Toluene-d_8	98
4-Bromofluorobenzene	95

[a] Priority Pollutant Compounds
[b] F-list Compound

Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and Reporting Limits (RL)

Method: Volatiles by 8260

Analyte	Ret Times (minutes)	Water (µg/L)			Soil (µg/Kg)		
		MDL	PQL	RL	MDL	PQL	RL
Acetone	5.39	3.93	12.51	10	9.46	30.13	10
Benzene	12.85	1.05	3.36	2	0.72	2.31	5
Bromobenzene	22.98	1.06	3.38	2	0.64	2.02	5
Bromochloromethane	11.09	0.88	2.79	2	0.66	2.10	5
Bromodichloromethane	16	0.97	3.10	2	0.85	2.71	5
Bromoform	22.12	1.13	3.59	2	0.73	2.32	5
Bromomethane	3.56	0.69	2.20	2	0.88	2.80	5
2-Butanone	10.64	5.86	18.66	10	3.65	11.64	10
n-Butylbenzene	25.55	0.75	2.38	2	0.65	2.08	5
sec-Butylbenzene	24.5	0.36	1.14	2	0.65	2.07	5
tert-Butylbenzene	27.08	0.44	1.41	2	0.73	2.33	5
Carbon Disulfide	5.44	2.49	7.92	2	1.54	4.91	5
Carbon Tetrachloride	12.08	1.05	3.35	2	1.06	3.36	5
Chlorobenzene	20.49	0.80	2.54	2	0.76	2.43	5
Chloroethane	3.74	1.09	3.47	2	0.98	3.12	5
Chloroform	11.41	1.18	3.76	2	1.00	3.17	5
Chloromethane	2.87	1.01	3.23	2	1.04	3.31	5
2-Chlorotoluene	23.33	0.96	3.04	2	0.82	2.63	5
4-Chlorotoluene	23.57	1.13	3.59	2	0.51	1.63	5
Dibromochloromethane	19.35	0.84	2.68	2	0.74	2.34	5
1,2-Dibromo-3-chloropropane	27.16	1.64	5.24	2	1.13	3.59	5
1,2-Dibromoethane	19.56	0.79	2.51	2	0.66	2.11	5
Dibromomethane	15.6	0.79	2.53	2	0.82	2.61	5
1,2-Dichlorobenzene	25.66	0.82	2.61	2	0.63	2.00	5
1,3-Dichlorobenzene	24.77	0.66	2.11	2	0.58	1.85	5
1,4-Dichlorobenzene	24.95	0.83	2.65	2	0.74	2.37	5
Dichlorodifluoromethane	2.56	0.72	2.28	2	1.03	3.29	5
1,1-Dichloroethane	8.13	1.49	4.75	2	0.94	3.00	5
1,2-Dichloroethane	13.22	0.96	3.07	2	0.66	2.11	5
1,1-Dichloroethene	5.08	0.93	2.95	2	1.38	4.40	5
cis-1,2-Dichloroethene	10.21	0.92	2.93	2	0.80	2.54	5

Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and Reporting Limits (RL)

Method: Volatiles by 8260

Analyte	Ret Times (minutes)	Water (µg/L)			Soil (µg/Kg)		
		MDL	PQL	RL	MDL	PQL	RL
trans-1,2-Dichloroethene	6.81	1.14	3.63	2	0.75	2.39	5
1,2-Dichloropropane	15.33	1.17	3.74	2	0.48	1.54	5
1,3-Dichloropropane	18.98	1.31	4.16	2	0.67	2.12	5
2,2-Dichloropropane	10.01	0.64	2.05	2	1.01	3.23	5
1,1-Dichloropropene	12.25	1.06	3.37	2	0.79	2.51	5
cis-1,3-Dichloropropene	17.03	0.94	2.98	2	0.80	2.55	5
trans-1,3-Dichloropropene	18.3	0.85	2.71	2	0.58	1.83	5
Diisopropyl ether	8.25	1.35	4.31	2	0.87	2.77	5
Ethylbenzene	20.67	0.80	2.53	2	0.79	2.51	5
Hexachlorobutadiene	28.85	(*)	(*)	2	0.81	2.58	5
2-Hexanone	19.17	3.74	11.91	10	3.33	10.61	10
Isopropylbenzene	22.37	0.74	2.35	2	0.60	1.92	5
4-Isopropyltoluene	24.78	0.71	2.26	2	0.67	2.13	5
Methyl Iodide	5.41	0.73	2.34	2	1.57	4.99	5
4-Methyl-2-pentanone	17.44	3.36	10.70	10	2.31	7.37	10
Methyl-t-butyl ether	6.83	1.46	4.65	2	0.94	2.99	5
Methylene chloride	6.27	1.51	4.81	2	1.03	3.26	5
Naphthalene	29.09	(*)	(*)	2	0.91	2.91	5
n-Propylbenzene	23.15	0.66	2.09	2	0.61	1.94	5
Styrene	21.74	1.00	3.20	2	0.53	1.68	5
1,1,1,2-Tetrachloroethane	20.69	0.88	2.80	2	0.96	3.06	5
1,1,2,2-Tetrachloroethane	23.12	1.33	4.24	2	0.69	2.19	5
Tetrachloroethene	18.66	0.57	1.81	2	0.72	2.30	5
Toluene	17.58	0.76	2.41	2	0.68	2.16	5
1,2,3-Trichlorobenzene	29.53	1.16	3.70	2	0.84	2.66	5
1,2,4-Trichlorobenzene	28.64	1.15	3.66	2	0.87	2.78	5
1,1,1-Trichloroethane	11.72	1.18	3.75	2	1.16	3.68	5
1,1,2-Trichloroethane	18.66	0.93	2.97	2	0.57	1.82	5
Trichloroethene	14.66	0.64	2.05	2	0.67	2.12	5
Trichlorofluoromethane	4.12	1.25	3.98	2	1.372	4.37	5
1,2,3-Trichloropropane	23.19	1.43	4.56	2	1.14	3.63	5
1,1,2-Trichloro-1,2,2-Trifluoroethane	5.01	0.89	2.83	2	1.46	4.64	5
1,2,4-Trimethylbenzene	24.21	0.80	2.53	2	0.62	1.99	5
1,3,5-Trimethylbenzene	22.37	0.74	2.35	2	0.58	1.85	5
Vinyl Acetate	8.38	5.62	17.91	10	4.08	12.98	10
Vinyl Chloride	3.01	0.69	2.21	2	1.08	3.45	5
o-Xylene	21.67	0.69	2.19	2	0.63	2.02	5
m,p-Xylene	20.91	1.67	5.31	4	1.33	4.24	10

(*)--The MDL for this compound is currently being reanalyzed.

Copy #: 8310-____

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYNUCLEAR AROMATIC HYDROCARBONS BY HPLC

GLA 8310 BG

Revision 2.1

Approved By:

Department Manager:		Date: 5-28-99
Quality Assurance Manager:		Date: 5/23/99
Laboratory Manager:		Date: 1/28/99

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of polynuclear aromatic hydrocarbon compounds (PNA's or PAH's) by high performance liquid chromatography (HPLC). This SOP is an interpretation of EPA method 8310. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, and non-aqueous solvent-soluble waste samples.

The holding time before extraction for water samples is 7 days and for soil samples 14 days. Samples are stored refrigerated (at ~4°C) prior to extraction - no additional preservation is needed. Sample extracts are stored under refrigeration and analyzed within 40 days of the extraction date.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

This method provides HPLC conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbon (PAH or PNA) compounds:

2.1 Samples for PNA analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, GLA SOP 3500 BG, sections 11.1 and 11.3). If the sample matrix is soluble in acetonitrile, a waste dilution may be performed.

2.2 Extracts are analyzed by HPLC. Aliquots of the extracts (10 µL) are injected and eluted using an acetonitrile/water gradient on a reverse-phase octadecylsilane column. All compounds, except acenaphthylene, in the effluent are detected by a fluorescence detector - acenaphthylene is detected by an ultraviolet (UV) detector.

2.3 Compounds that can be detected by this method include: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3,-cd)pyrene, 1-methyl-naphthalene, 2-methyl-naphthalene, naphthalene, phenanthrene, and pyrene.

2.4 The sensitivity of this method is very dependent on the level of interferences rather than instrumental limitations. The limits of detection represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest level possible. Gloves are worn when handling solvents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential health hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received into the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for hazardous sample management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interference, under the conditions of the analysis, by running method blanks. Sample extracts can become contaminated if they come in contact with contaminated glassware or syringes used in the extraction and preparation of samples with high concentrations of analytes. Glassware is thoroughly washed, deionized water rinsed, and solvent rinsed as indicated in the glassware preparation SOP. Syringes are rinsed three times with acetone, methylene chloride and acetonitrile before each use. Glassware, syringes, and dilution solvent used in waste dilution extractions are stored separately from routinely used glassware.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 CO-EXTRACTED INTERFERENCES

Interferences co-extracted from the samples will vary considerably from source to source. The chromatographic conditions described allow for a unique resolution of the specific PNA/PAH compounds covered by this SOP. Other compounds, in addition to matrix artifacts, may interfere. An oily matrix will have an effect on the sensitivity of the procedure as well. Oily samples are typically diluted.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe may be rinsed out between samples with water or solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

For each HPLC instrument, an instrument maintenance logbook is kept . It contains the instrument name, beginning date and ending date of the Logbook on the front cover. This book will include all routine instrument maintenance, repairs and any instrument modifications. All entries must be dated and initialed.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each method. It has the method identification number on the outside cover. This contents of each book include:

- Copy of the GLA Quality Assurance Program manual.
- Copies of the GLA SOP and source methods.
- Copies of all calibration data.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Copies of accuracy and precision studies.
- Copies of all control limit studies.
- Surrogate standard recovery tabulations and control limits.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The names and concentrations of the internal standard and surrogate standard(s).

The following column headings are written at the top of each page, and may include:

- Data file name.
- Dates of extraction and analysis.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used - dilution, if any.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.)
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes and crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

5.4 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 3 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:

- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code(s) for the final solution(s). The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

6.0 QUALITY CONTROL

6.1 METHOD BLANKS AND SAMPLE SPIKES

For quality control, each water extraction batch contains a method blank (MB), and a blank spike (BS), and a blank spike duplicate (BSD). (An analytical batch does not contain more than 20 samples.) Deionized water is used for water method blanks and spikes.

Each soil extraction batch contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). Clean sand is used for soil method blanks (MB) and spiked blanks (LCS). Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

A surrogate compound is added to all samples, blanks, and spikes in an analytical batch.

6.2 CHECK STANDARD

Each day before analysis of samples begins, the calibration curve is verified using a check standard. (This standard is from a different source/vendor than the calibration standard.) The check standard is run and quantitated every 12 hours, or every 20 samples, whichever is more frequent. The chromatography of the check standard is evaluated for peak shape and co-elution problems. Each day, a successful Check Standard must be analyzed before sample analyses can begin. A successful check standard contains all analytes with 85-115% recovery. Corrective action must be taken for those analytes that fall outside these limits.

6.3 METHOD BLANK

No contaminants should be present in the blank above the method detection limit. If contaminants are found the blank and all related samples must be reanalyzed. If the blank contamination persists, the samples are re-extracted. A blank is extracted with every batch.

6.4 SURROGATE STANDARD

Surrogate standards are used to monitor the efficiency of the procedure. The surrogate standard for this method is 7,12-dimethylbenz(a)anthracene. The control limits for the surrogate are calculated as the average percent recovery plus/minus 3 standard deviations. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 MATRIX SPIKES

A blank spike and blank spike duplicates are analyzed with all samples. Spikes are run every 10 samples. Spike recoveries for all compounds are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery per matrix for a particular compound plus/minus 3 times the standard deviation.

6.6 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails.
- Contamination was present in the blank and in the sample.
- Recovery for the laboratory control sample outside of limits.

6.7 CONFIRMATION

The ultraviolet (UV) detector is used to confirm the presence of PNA/PAH's. GC/MS may be used for the confirmation of moderate to high levels of PNA/PAH's.

6.8 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8310 are queued under "EXTR" and "HPLC". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 CALIBRATION STUDY

A *calibration study determines the response factors (RFs) for analytes that are used for the* determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram. A minimum of 5 concentration levels is required (see Section 10.1.2).

A response factors (RF) is calculated by tabulating responses of each analyte against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression is used to establish the equation of the calibration curve for that particular compound: *peak area = slope x concentration + constant.* Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. (Surrogate standard is added at the same level as other compounds.)
- For each compound, calculate:
* $RF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
* *Average and standard deviation for RFs*
* $\%RSD = \frac{\text{standard deviation of RFs} \times 100}{\text{average RF}}$
- If the %RSD is less than 20%, the average RF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 85 and 115%.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the recoveries of 7 aliquots times the t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 aliquots is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if you inject 1µg/L of standard, the calculated MDL must be between 0.1 and 1 µg/L. A MDL study is done yearly.

Procedure summary:

- Analyze 7 replicates of low level standard (at or below lowest calibration level standard).
- Calculate standard deviation for the 7 replicates.
- MDL = standard deviation x 3.143.
- The calculated MDL must be less than the reporting limit.

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed annually, by new analysts, or when a new column is installed.

Procedure summary:

- Analyze the check standard 3 times over a 3 day (72 hour) period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time ± 3 × standard deviation. (A standard deviation of 0.01 may be used if the calculated standard deviation is less than 0.01 minutes.)
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy (demonstration of proficiency).

Procedure summary:

- Analyze 4 replicate standards or spiked extracts for both water and soil matrices.
- Recoveries of each compound must be between 80 and 120%.
- The %RSD of each set must be less than 20%.

9.0 EQUIPMENT

9.1 High performance liquid chromatograph (HPLC), consisting of:

- Pumping system - capable of gradient chromatography - Waters 510, Hewlett-Packard 1050, or equivalent.
- Sample injector/controller - Waters WISP 712, Hewlett-Packard 1050, or equivalent.
- Analytical column - reverse-phase HC-ODS Sil-X, 5 µ particle size, 25 cm × 2.6 mm ID, or VYDAC C-18, 5 µ particle size, 25 cm x 4.6 mm ID (Perkin Elmer no. 089-0716, or equivalent).
- Ultraviolet (UV) detector - capable of detection at 254-nm - Waters 486, Hewlett-Packard 1050, or equivalent.
- Fluorescence detector - for excitation at 280 nm and emission greater than 389 nm - Waters 470, Hewlett-Packard 1046A, or equivalent.
- Data collection and analysis system.

9.2 Glass syringes, various sizes.

9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOLUTIONS

10.1.1 Stock Standard Solutions:

a. Commercially prepared stock standards are purchased from various suppliers. Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Two different sets of standards are used for this analysis. One set of standards is used for instrument calibration, and contain the PNA/PAHs at several concentrations. The other set of standards is used for spiking of blanks (BS/BSD) and samples (MS/MSD), and has all analytes at the same concentration levels. In addition, the second set of standards is used for the preparation of the daily check standard.

b. The stock standards are transferred into Teflon-sealed screw-cap vials. The standards are stored refrigerated (at ~4°C) and protected from light. Stock standards are checked for signs of degradation or evaporation.

c. Stock standard solutions are replaced after one year, or sooner if comparison with check standard indicates a problem.

10.1.2 Calibration Standards:

a. Calibration standards at a minimum of five concentration levels are prepared through dilution of the stock standards with acetonitrile. One of the standards is at a concentration near, but above, the instrument detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. Due to the varying response of the target compounds, more than five points are analyzed. The initial calibration consists of of standards at 5.0, 10, 50, 100, 500, 1000, 2000, 3000, 5000, 7000, and 10000 ng/ml. The calibration stock standard must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

b. Calibration standards are made up of 4 ampules which are combined to contain all 18 target compounds and the surrogate. The first ampule contains a PNA mix that contains all (16) target compounds except the surrogate 7,12-dimethylbenz-(a)anthracene, 1-methylnaphthalene, and 2-methyl-naphthalene. The other 3 ampules are for each of the three remaining compounds (AccuStandard no's. 4-8743, 4-0567, 4-8162, and 4-8366).

The typical concentrations found in the ampules are:

PNA (PAH) Mix	2000 µg/mL
7,12-Dimethylbenz(a)anthracene	1000 µg/mL
1-Methylnaphthalene	1000 µg/mL
2-Methylnaphthalene	1000 µg/mL

Prepare a 50-mL aliquot of 10,000 µg/L solution by adding 500 µL of 7,12-dimethylbenz(a)anthracene, 1-methylnaphthalene and 2-methylnaphthalene. Add 250 µL of the PNA mix and bring up to volume with acetonitrile. Use this 10,000 µg/L stock solution to prepare a set of standards which range from 5.0 ppb to 7,000 ppb and using the 10,000 ppb stock solution as the final standard.

10.1.3 Surrogate Standards: This analysis is monitored for the performance of the extraction, cleanup (if necessary), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with a surrogate compound. 7,12-Dimethylbenz(a)anthracene is used as the surrogate (AccuStandard no. 4-0567 or Restek no. 31286), at a concentration of 100 µg/mL.

10.1.4 Spike Standards: Restek SV CAL Mix #5 (no. 31011, 16 PNA/PAH compounds), 1-methylnaphthalene (Restek no. 31283), and 2-methylnaphthalene (Restek no. 31285), at a concentration of 100 µg/mL.

10.2 STANDARD DILUTIONS

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.
C_2 = desired or calculated concentration of the working standard.
V_1 = volume of the stock standard diluted.
V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Opening of the standard is documented in the Standard Log.

10.4 WORKING STANDARD

Standards are prepared in acetonitrile:

- Determine volumes of stock and working standard required.
- Fill volumetric flask about ¾ full with solvent.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to amber vials with Teflon caps.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date prepared.
  - Purpose (method).
  - Initials.
  - Expiration date.
  - GLA code.

Preparations are documented in the Standard Log.

NOTE: A 5µL aliquot of a 10 ng/µL working standard is equivalent to 50 ng:
10 ng/µL × 5 µL = 50 ng

The GLA code is an alphanumeric sequence used to track standard preparations within the lab in a method-type-date-(letter) format. For example, "8270 CAL 020599 A" indicates method 8270, calibration standard, prepared 2/5/99, first concentration level (A).

10.5 REAGENTS

10.5.1 Reagent water - water in which an interference is not observed at the method detection limit of the compounds of interest (PNA/PAHs).
10.5.2 Acetonitrile - HPLC grade, or equivalent.
10.5.3 Helium - ultra-high purity grade, for sparging mobile phases.
10.5.4 Compressed air or nitrogen - for operation of pneumatic instrumentation/equipment.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions. Appendix A contains example chromatograms for this method.

11.1 HPLC Gradient Programs: The solvent gradient program used for the analysis of PNAs are as follows:

Waters Systems

Flow Rate: 2.0 ml/min.
Gradient:

Time (minutes)		% Acetetonitrile	% Water
Initial		50	50
3.0		50	50
9.0	linear to	60	40
17.0	linear to	75	25
27.0	linear to	90	10
28.0	linear to	91	9
29.0	linear to	50	50
45		50	50

Hewlett Packard System:

Flow Rate: 1.25 ml/min
Gradient:

Time		% Acetonitrile	% Water
Initial		50	50
5.0		50	50
10.0	linear to	60	40
17.0	linear to	75	25
27.0	linear to	90	10
28.0	linear to	91	9
35.0	linear to	100	0
35.1	linear to	50	50
40.0		50	50

11.2 The analyst plans the sequence, enters the sample numbers into the sequence file, and records all the needed information into the Run Log. The daily sequence will be as follows:

A. *Check standard (contains all compounds with each RF ≤ 15% difference from initial calibration).*
B. Acetonitrile blank.
C. Samples or QC samples (number of samples/QC based on 12 hour clock).
D. Check standard.
E. Repeat steps C and D.

11.3 The chromatography of the check standard is evaluated for peak shape and co-elution problems. The calibration check standard is quantitated and all QC criteria must be met before analysis of samples can begin. All reportable samples and spikes must be bracketed by valid check standards. Any samples not bracketed must be reanalyzed.

11.4 HPLC analysis - the sequence of steps necessary to clean, equilibrate, and perform instrumental analysis follows:

11.4.1 Daily Maintenance:

- Check helium tank pressure.
- Check compressed air tank pressure.
- Fill acetonitrile reservoir.
- Fill water reservoir.
- De-gas newly filled solvents for approximately 15 minutes.
- Fill needle wash bottles with acetonitrile.
- Dispose of solvent waste in flammable solvent waste drums.
- Remove check standard and all samples to be run from the refrigerator and allow to come to room temperature.

11.4.2 Analyze samples:

a. Operate gradient function - necessary to prepare the instrument for the initial conditions to run the samples:
   - On the Gradient controller, press [OPERATE GRADIENT] [8] [ENTER] [ENTER] [2] [ENTER].
   - The instrument should run without sample injection at this setting for approximately 5 minutes.

   A typical gradient profile used is 50% acetonitrile initially for 5 minutes, linear gradient to 100% acetonitrile over 25 minutes, with a mobile phase linear velocity of 2 mm/sec (*e.g.* 1.5 mL/min for a 4.6 mm ID column).

b. Create the sequence - necessary to collect and retrieve data from samples that have been run - in the GCTop:
   - Select [SEQUENCE-SAVE].
   - Enter the date you want the data saved under.
   - Select [EDIT SEQUENCE LOG].
   - Enter the amount of samples that will run with the appropriate method and individual sample information. Select [MORE] to enter additional information such as sample dilutions and printing options (select "NONE" as a printing option so the sample information will not print during the run). When all information has been entered choose [OK].
   - Select [LOAD AND RUN SEQUENCE].
   - Choose [OK] at the prompts, choose and enter correct date.
   - When prompt reads "READY TO INJECT", run can begin.

c. Starting the run on the WISP - this will inject the samples and begin the run:
   - Open the door and place samples in the carousel.
   - While door is still open press [SYS MES] [7] [7] [ENTER], then the last sample number in the carousel, [ENTER].
   - Close the door, press [RUN/STOP], the red light will move from STOP to RUN.
   - To pause WISP during a run, open door - this will prevent the next sample from being injected.

11.4.3 Generate reports - reports consist of sample results and corresponding chromatograms:

a. Load data file - bring up the file to be quantitated. The samples run on LC-1 will be found in "c:\hpchem\5\data\date" run. The samples run on LC-2 will be found in "c:\hpchem\6\data\ date" run.

b. Update retention times - Update the retention time of the first check standard run before that sample. To do this select [TOOLS] [EASYID], underline each peak for the appropriate compound. After updating and saving all peak changes, choose [FILE] [SAVE METHOD] to save to the method. Quantitate all samples run after the check standard with that check standards retention times. When subsequent check standard appears, repeat the above procedure.

c. Quantitate results - After updating the proper check standard retention times, pull up the sample file you wish to quantitate. Be sure the correct method is loaded and then choose [CALCULATE AND GENERATE REPORT]. If any compounds required manual integration, select [QUANT] [Q EDIT QUANT RESULT]. Every attempt should be made to avoid the use of manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of the calibration standards constitutes fraud, and is strictly forbidden.

d. Print results - To print results that have been quantitated, select [TOOLS] [DO LIST] [SUMMARY QUANT W/OUT CALCULATIONS], and highlight those to be printed. This will print the quantitated results with any Qedit changes made.

11.4.4 Calculations - Divide by factors necessary to convert report results (instrument report values in ppb) to reportable units. These calculations assume a starting volume of 1 L of sample for waters and 30 g of sample for soil samples.

Waters in ug/L:	Result / 100
Illinois Soils in µg/kg:	Result / 3
Wisconsin Soils in ug/kg :	Result / 3 × Dry Weight

If the sample volume or weight is less than the assumed starting value, then a dilution factor is applied to the above calculations.

11.5 QC Calculations:

11.5.1 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.2 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

11.6 If all the QC requirements for the day have been met, the samples have been analyzed at the proper dilution, and analytes found in the samples (hits) have been confirmed, the results are ready for peer review.

11.7 Reporting Results - Once analysis is completed for a group of samples and all QC measures have been satisfied, sample results can be recorded on the report worksheets. The analyst records the date of analysis for the sample. When recording the results on the worksheet the analyst circles the compound with a positive result, and the ND is crossed out. Next to the ND, the concentration found in the sample is recorded. After an analyst has recorded the results for each sample he/she signs, and dates the first reporting page for that analysis. The analyst also records results of the spike and spike duplicate data on the QC sheet attached to the report.

11.8 LIMS Reporting - All sample results should be downloaded into the LIMS on a regular basis.

11.8.1 Batching - must be done before results can be transferred to LIMS. There are several ways to batch samples. One way is to clone the extraction batch so that the analysis batch corresponds to the extraction batch:

[BATCHES] - [EDIT] - [BY BATCH] - F8

Queue = type HPLC (all caps)
Batch Rule = press [F2] , enter
Batch Queue = type EXTR (all caps)
Batch = the numerical extraction batch that is being cloned.

Press [F4] twice, the extraction batch will now be given an HPLC batch number as well and the samples are ready to be transferred (posted) to LIMS.

11.8.2 Do List - done in Enviroquant, this is the process of converting the data files collected to .CSV files in the C drive. This can only be done after the samples results have been batched:

select [TOOLS]
[DO LIST]
[QUANT TO FORMS W/O CALC] [OK]
Highlight the samples to be transfered and choose [ADD] [PROCESS].

In order for the samples to be converted, the correct format must be used when entering sample information in the sequence including any dilution factors used. The following are examples for method 8310 water, soil, SPLP, and method 610:

GLA sample #|HPLC|8310WA|OK
GLA sample #|HPLC|8310SA|OK
GLA sample #|HPLC|8310PA|OK
GLA sample#|HPLC|610|OK.

11.8.3 Posting - transferring the .CSV files from the C drive to the LIMS drive. Can only be done at the Department Manager's terminal:

From FILE MANAGER, the files will be in C:\posted. Copy the files contained in "posted" to the HPLC LIMS drive. After the copies have been made, the files in "posted" can then be deleted.

11.8.4 Parsing - done in LIMS to process the .CSV files sent by POSTING.

select [SYSTEM] [PARSERS]
Program = press [F2] and chose HPCHEMST
Action = type START (all caps)
Cycle = type [1]
Press [F4] to commit and [ENTER] at the prompt.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

Some troubleshooting suggestions (problem - possible remedy):

- Broad peaks or poor peak resolution - change guard column.
- High pressure - change guard column.
- No or low pressure - prime pump, check for leaks.
- Noisy baseline - check source.
- No peaks - check the gradient program.
- Increased retention times - flow rate decreasing, check for leaks.
- Upon opening door of WISP tray will not release - check air tank.

13.0 REFERENCES

13.1 Testing Methods for the Evaluating of Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Methods 3510B, 3550B, 8000B, and 8310.

13.2 Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters, EPA-600/4-82-025, US. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 (September 1982).

13.3 EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons), Report for EPA Contract 68-03-2624.

13.4 EPA 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule (October 26, 1984).

13.5 Interpretation of Percent Recovery Data, L.P. Provost and R.S. Elder, American Laboratory, vol. 15, pp. 58-63 (1983).

13.6 Great Lakes Analytical Quality Assurance Program manual.

13.7 Great Lakes Analytical Chemical Hygiene Plan.

13.8 Great Lakes Analytical SOP for Login Department.

13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

APPENDIX A.

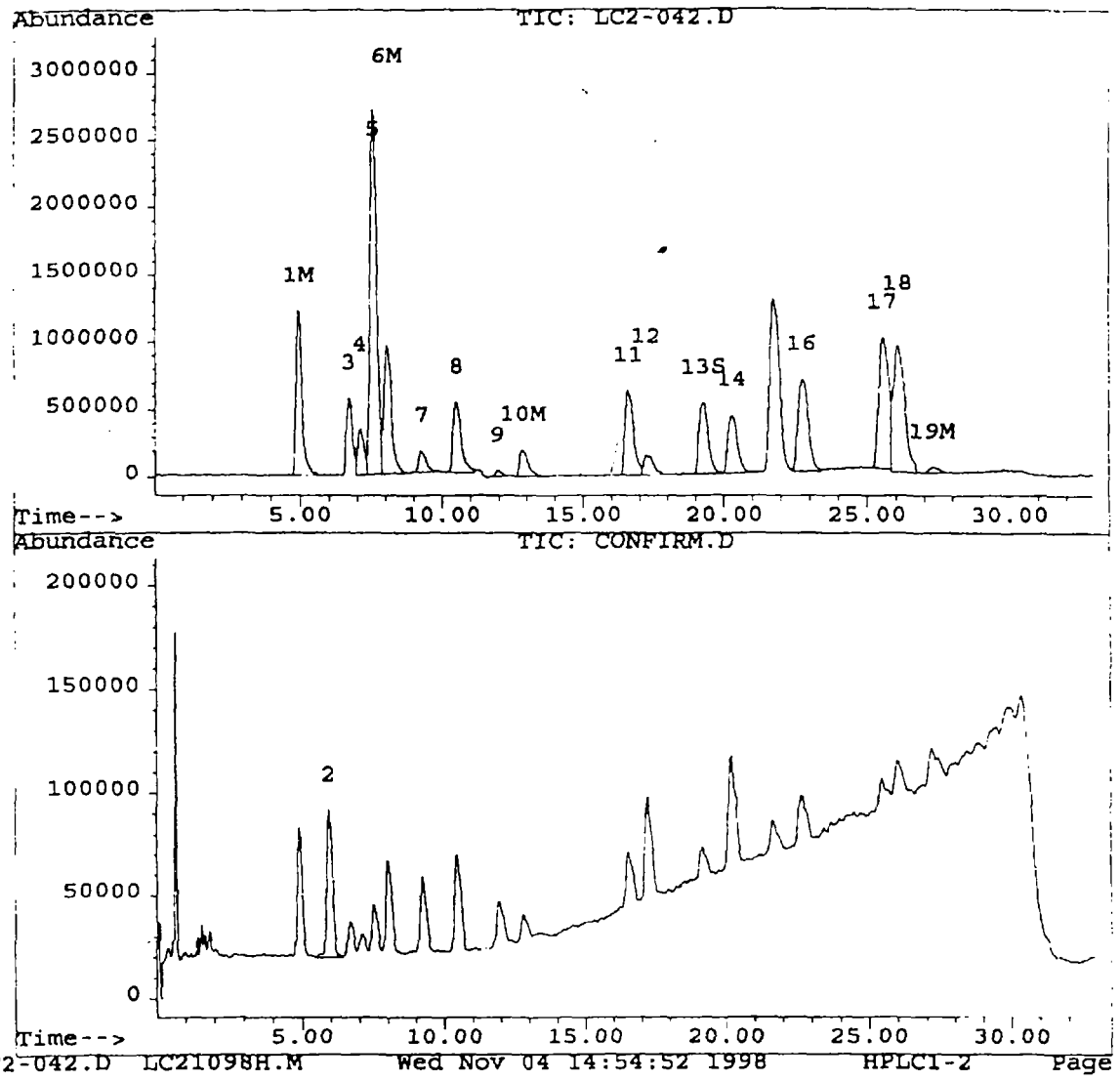
EXAMPLE CHROMATOGRAMS.

Peak No.	Compound	Approximate R.T. (min)	Typical Response, Fluorescence (area counts x 10^6)
1	Naphthalene	4.9	17.8
2	Acenaphthalene	5.9	1.0†
3	1-Methylnapthalene	6.7	8.9
4	2-Methylnaphthalene	7.1	5.2
5	Acenaphthene	7.5	43.7
6	Fluorene	8.0	16.9
7	Phenanthrene	9.3	2.8
8	Anthracene	10.5	10.5
9	Fluoroanthene	12.0	0.8
10	Pyrene	12.9	4.5
11	Benzo(a)anthracene	16.6	13.3
12	Chrysene	17.2	3.5
13	7,12-Dimethylbenz(a)anthracene	19.3	11.9
14	Benzo(b)fluoranthene	20.3	10.0
15	Benzo(k)fluoranthene	21.7	<0.1
16	Benzo(a)pyrene	22.7	17.2
17	Dibenzo(a,h)anthracene	25.5	22.7
18	Benzo(g,h,i)perylene	26.1	25.8
19	Indo(1,2,3-cd)pyrene	27.3	1.0

† Ultraviolet (UV) detector response.

Top chromatogram: Fluorescence detector

Bottom chromatogram: *Ultraviolet detector*



DATA REVIEW

		YES	NO	CA	FLAG
1	Check standard recoveries within ± 15 % ?				
(8081) 1b	Prime and blank run?				
(8081) 1c	Endrine DDT breakdown < 15 % ?				
(8270) 1d	DFTPP tune evaluated and passing?				
(8270) 1e	SPCC average response factor > 0.050 ?				
(8270) 1f	CCC % deviation > 20 % ?				
(8270) 1g	Internal recoveries within 50-100 % ?				
2	Method blank recoveries < reporting limits?				
3	LCS within control limits?				
4	MS/MSD within control limits?				
5	All surrogate recoveries within control limits?				
6	All hits out of cal range diluted and re-analyzed?				
7	All sample holding times met?				
8	No transcription errors?				
9	No calculation errors?				

COMMENTS:

Analyst review signature: _____ Date: _____

Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and Reporting Limits (RL)

Method: PNAs by 8310

Analyte	Water (µg/L)			Soil (µg/Kg)		
	MDL	PQL	RL	MDL	PQL	RL
Naphthalene	0.017	0.060	3	0.87	3.08	30
Acenaphthylene	0.582	2.065	4	91.34	323.62	200
Acenaphthene	0.028	0.099	5	6.85	24.28	30
Fluorene	0.029	0.104	1	0.91	3.24	30
Phenanthrene	0.037	0.130	0.3	1.62	5.73	30
Anthracene	0.019	0.069	0.2	0.40	1.28	30
Fluoranthene	0.016	0.057	1	4.76	16.88	30
Pyrene	0.009	0.032	1	4.32	15.32	30
Benzo (a) Anthracene	0.038	0.136	0.1	0.48	1.69	30
Chyrsene	0.020	0.070	0.05	1.55	5.50	30
Benzo (b) Fluoranthene	0.010	0.033	0.02	0.38	1.21	30
Benzo (k) Fluoranthene	0.010	0.037	0.05	0.85	3.02	30
Benzo (a) Pyrene	0.023	0.081	0.05	0.67	2.38	30
Dibenzo (a,h) Anthracene	0.019	0.059	0.02	0.88	3.13	30
Benzo (g,h,i) Perylene	0.020	0.069	0.06	0.94	3.32	30
Indeno (1,2,3-cd) Pyrene	0.017	0.061	0.2	4.53	16.06	30